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ATMOSPHERIC EMISSIONS FROM WET-PROCESS PHOSPHORIC ACID MANUFACTURE

Cooperative Study Project
Manufacturing Chemists' Association, Inc.
and
Public Health Service

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PREFACE

To provide reliable information on the nature and quantity of emissions to the atmosphere from chemical manufacturing, the Public Health Service, United States Department of Health, Education, and Welfare, and the Manufacturing Chemists' Association, Inc., entered into an agreement on October 29, 1962, to study emissions from selected chemical manufacturing processes and to publish information that would be helpful to air pollution control and planning agencies and to chemical industry management.[*] Direction of these studies is vested in an MCA-PHS Steering Committee, presently constituted as follows:

Representing PHS	Representing MCA
Stanley T. Cuffe[†]	Willard F. Bixby[†]
Robert L. Harris, Jr.	Louis W. Roznoy
Dario R. Monti	Clifton R. Walbridge
Raymond Smith	Elmer P. Wheeler

Information included in these reports describes the range of emissions during normal operating conditions and the performance of established methods and devices employed to limit and control such emissions. Interpretation of emission values in terms of ground-level concentrations and assessment of potential effects produced by the emissions are both outside the scope of this program.

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[*] Reports in this series to date are Atmospheric Emissions from Sulfuric Acid Manufacturing Process, Public Health Service Publication No. 999-AP-13, Atmospheric Emissions from Nitric Acid Manufacturing Processes, Public Health Service Publication No. 999-AP-27, and Atmospheric Emissions from Thermal-Process Phosphoric Acid Manufacture, Public Health Service Publication No. 999-AP-48, and Atmospheric Emissions from Hydrochloric Acid Manufacturing Processes, National Air Pollution Control Administration Publication No. AP-54.

[†] Principal representative.

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USE AND LIMITATIONS OF THE REPORT

This report, one of a series concerning atmospheric emissions from chemical manufacturing processes, is designed to provide information on phosphoric acid manufactured by the wet process.

Background information describing the importance of the wet-process phosphoric acid industry in the United States is included. Basic characteristics of the industry are discussed, including growth rate in recent years, uses for the product, and number and location of producing sites.

The only important wet-process phosphoric acid manufacturing procedure in the United States today involves treatment of phosphate rock with sulfuric acid. Descriptions are given of the most commonly used process variations that involve the formation of calcium sulfate dihydrate, since these account for the greater part of U.S. production. Process information includes: discussion of factors that affect the quantity of emissions, the normal range of emissions, and methods for controlling emissions. Supplemental material provides detailed descriptions of emission-sampling and analytical methods.

The emission data used herein represent results from approximately 20 percent of the present number of establishments.* Most of the data are derived from a series of stack sampling programs conducted during 1966 and 1967 by the Public Health Service at ten establishments, which produce about 48 percent of the wet-process phosphoric acid made in the United States.

Although this report is a technical review prepared primarily for public officals concerned with the control of air pollution, it is expected that it will also be helpful to chemical plant management and its technical staff. This report should be reviewed at intervals to determine whether revision is necessary.

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*Establishment - A works having one or more wet-process phosphoric acid plants or units, each being a complete production entity.

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ATMOSPHERIC EMISSIONS FROM WET-PROCESS PHOSPHORIC ACID MANUFACTURE

SUMMARY

WET-PROCESS PHOSPHORIC ACID MANUFACTURE

In 1966, the production of wet-process phosphoric acid, expressed as P_2O_5, was approximately 3.5 million tons. Much of this was produced as 54 percent P_2O_5, and virtually all of it was used to produce various phosphate fertilizers. Fertilizers are produced by treating phosphate rock with wet-process phosphoric acid to form triple superphosphate, TSP, or by reacting phosphoric acid with anhydrous ammonia to form ammonium phosphates, especially diammonium phosphate, DAP.

Wet-process acid is produced by treating fluorapatite [$Ca_{10}(PO_4)_6F_2$] or phosphate rock, with sulfuric acid. Phosphoric acid is formed, calcium sulfate is precipitated and filtered off, and the acid is concentrated from about 32 percent P_2O_5 to about 54 percent P_2O_5 Phosphate rock is found all over the world and varies in physical and chemical properties. An acid plant must be designed for the rock it will process. Although sulfuric acid of any strength will cause the desired reaction, in practice, 98 percent acid is used.

POTENTIAL EMISSIONS FROM UNIT PROCESSES

Phosphate rock must be finely ground to react properly with sulfuric acid, and standard control equipment is normally used to prevent objectionable dust emissions.

The emissions of most concern are fluoride compounds liberated from the rock by the sulfuric acid. These consist of hydrogen fluoride, silicon tetrafluoride, and some products of reaction and decomposition of the latter. Most phosphate rock contains 3.5 to 4 percent fluorine, and half of this may be volatilized in the processing. This represents a large potential source of pollution.

to p. 2

Fluoride emissions may occur from exposed surfaces of reaction slurry, aqueous solutions of fluorine compounds, and any evaporation process. Thus, reactors, open-slurry launders, flow splitter boxes, evaporators, filters, and sump tanks are potential emission sources.

The quantity of gaseous fluorides generated in the digester ranges from 0.037 to 2.16 pounds per ton of acid produced. The level of gaseous fluorides evolved from the filter ranges from 0.011 to 0.63 pound per ton of acid, while as much as 0.26 pound of gaseous fluoride per ton of acid is generated in the sump and associated vents. Total particulate emissions amount to approximately 0.20 pound per ton of acid for filter operations, and as much as 11 pounds per ton for digester operations. Only a small portion, i.e., 3 to 6 percent of the particulate emissions, consists of fluorides. Fluoride emissions may occur from gypsum ponds, and the quantity of emissions depends on pH and chemical composition of the pond and upon temperature and wind speed. Data for one gypsum pond given in this report indicate a possible fluoride emission of 0.4 to 1.8 pounds of fluoride per acre per day, depending on temperature.

CONTROL OF EMISSIONS

Because the principal atmospheric contaminants generated in the process are gaseous fluorides, vapor scrubbing is universally employed to control emissions. Specific devices used for control include venturi scrubbers, impingement scrubbers, and various kinds of spray towers. Fluoride removal efficiency of these devices varies widely, and staging may be required for satisfactory control. Plugging, or difficulty in removing precipitates and dust, may also be experienced.

Tables in Appendix A show the results of MCA-PHS stack tests on ten wet-process phosphoric acid plants in various parts of the country are For nine of these plants, the range of gaseous fluoride emissions from various types of collectors was 0.006 to 0.17 pound of fluoride per ton of P_2O_5 produced. The concentration range of gaseous fluorides in the gases from collectors was 3 to 40 parts per million, and 0.0011 to 0.0147 grain per standard cubic foot for eight of the ten plants. Public Health Service stack-test data agree reasonably well with results from plant questionnaires and information from miscellaneous sources, both of which are tabulated in Appendix A.

The spray cross-flow, packed scrubber is reported to be capable of over 99 percent efficiency in the removal of pollutants. The usual exit concentration range for this type of scrubber is 0.001 to 0.01 grain of fluoride per standard cubic foot, according to stack samples taken by Public Health Service personnel for this project.

Scrubber efficiency is affected substantially by the loading of the gas stream. Heavy loading enhances scrubber efficiency, and light loading reduces scrubber efficiency. Therefore, scrubber-exit-gas concentration is a better indicator of overall plant emission control than is scrubber efficiency. The best criterion of plant performance is the weight of emission per ton of P_2O_5 produced.

A summary of plant tests made for this project shows the range of concentration of gaseous fluoride emissions after the scrubber.

GASEOUS FLUORIDE

Control device	Scrubber efficiency, %	Scrubber exit loading, gr/scf	Emissions, lb/ton P_2O_5 produced
Company-constructed spray chambers	55 - 75	0.0026 - 0.090	0.072 - 0.63
Venturi scrubbers	84 - 96	0.010 - 0.023	0.027 - 0.047
Cyclone spray towers	90 - 95	0.0016 - 0.003	0.047 - 0.082
Spray cross-flow packed scrubber	60 - 93	0.001 - 0.014	0.006 - 0.17

Performance data on the first two control devices mentioned in the preceding list relate to the treatment of digester emissions only. Their performance for emissions other than gaseous emissions was as follows:

Control device	Pollutant	Scrubber exit loading, gr/scf	Scrubber efficiency, %	Emissions, lb/ton P_2O_5 produced
Company-constructed spray chamber	Particulate	0.04 - 0.47		0.28 - 0.50
	Insoluble F	0.0009 - 0.0011		0 - 0.008
	Soluble F	0.0003 - 0.014		0.0075 - 0.094
Venturi scrubber	Particulate	0 - 0.009	above 98	0. - 0.3
	Insoluble F	none found	about 100	none found
	Soluble F	0.0009	94 - 97	0.003

EMISSION GUIDELINES

tabulated.

The major source of gaseous fluoride emissions in wet-process phosphoric acid plants is the digester. Only trace quantities of particulate fluorides are normally present in exit gases from digesters and filters, and these can be removed effectively by scrubbing.

The technology for controlling gaseous fluoride emissions by water scrubbing has been available for many years. By proper attention to mechanical design and good mass-transfer practice, such a unit can be built and operated to obtain almost any desired reduction in gaseous fluoride emissions. Such scrubbers are capable of operating with collection efficiencies of over 99 percent. The usual exit concentration for this type of scrubber ranges from 0.001 to 0.01 grain of fluoride per standard cubic foot or 0.006 to 0.17 pound of fluoride per ton of P_2O_5 produced.

It should be practical to operate wet-process phosphoric acid plants within the above ranges if plants are designed to prevent or collect

emissions, if modern scrubbers are used, and if attention is directed toward proper operation and maintenance of both process and emission control equipment.

Proper attention to air pollution control would dictate that the water scrubbers be started before process equipment and operated for a brief period after plant shutdown.

GROWTH OF WET-PROCESS PHOSPHORIC ACID INDUSTRY

HISTORICAL BACKGROUND

The agricultural benefits gained by mixing materials such as bone and bird guano with the soil have been observed from ancient times. Gahn, in 1669, was perhaps the first to associate the phosphorous content of such materials with their ability to fertilize the soil.[2] Liebig, in 1840, suggested solubilizing the phosphorous content of bones by treatment with sulfuric acid.[3] By this time, population growth had caught up with the ability of European soil to produce, and this furnished incentive for the extension of Liebig's ideas into various ways of treating phosphorus-bearing materials with strong acids. This activity soon led to the idea of treating phosphate rock with phosphoric acid instead of sulfuric acid. The phosphoric acid, it was discovered, could be made by decomposing phosphate rock with sulfuric acid and filtering off the resulting calcium sulfate. Thus, by 1872, wet-process phosphoric acid was being made in Germany and used in manufacturing triple superphosphate.[4] This work was taken up in America, and, by 1890, a triple-superphosphate plant was operating in Baltimore.[2]

Early wet-process phosphoric acid plants were simple; they involved batch treatment of phosphate rock with dilute sulfuric acid. The physical chemistry involved was poorly understood, and process controls were rudimentary. Filtration difficulties resulted in losses of phosphate in the calcium sulfate filter cake.

The control difficulties of batch processing led to early attempts to devise a continuous wet-acid process. The Dorr weak-acid process was an important contribution developed before 1930. It used a continuous reaction system, but was capable of producing acid no more concentrated than 20 to 22 percent.[5]

The principle of the Dorr strong-acid process, developed about 35 years ago, is employed in the production of most wet-process acid today. This process involves adding ground-rock feed and sulfuric acid to a large stream of recirculated reaction slurry. Compared to the weak-acid process, this process enhances yield and filterability by minimizing local changes in sulfate ion concentration, by furnishing system capacitance, and by furnishing proper sites for crystal growth. The acid filtrate is 30 to 32 percent P_2O_5.

Several variants of the above process are employed in modern plants to separate calcium sulfate as gypsum crystals. In addition to the Dorr strong-acid process, the Prayon[2] and St. Gobain [2,4] processes are used. All produce an acid filtrate containing about 30 to 32 percent

P_2O_5: process complications prevent production of stronger acid by these processes. Concentration of this filtrate to about 54 percent P_2O_5 is accomplished by evaporation in vacuum evaporators or by submerged combustion. Growth of the industry is shown in Table 1.

Table 1. GROWTH OF WET-PROCESS PHOSPHORIC ACID INDUSTRY IN UNITED STATES[1]

Year	Production of 100 % P_2O_5, tons
1941	131,000
1942	119,000
1943	127,000
1944	141,000
1945	133,000
1946	165,000
1947	175,000
1948	221,000
1949	245,000
1950	299,000
1951	338,000
1952	389,000
1953	496,000
1954	631,000
1955	775,000
1956	812,000
1957	936,000
1958	1,033,000
1959	1,141,000
1960	1,325,000
1961	1,409,000
1962	1,577,000
1963	1,957,000
1964	2,275,000
1965	2,837,000
1966	3,533,000

CURRENT PRODUCTION AND USES

In spite of the large absolute value of wet-process phosphoric acid production, the yearly rate of increase in production is maintained because of the soaring demand for concentrated or high-strength fertilizers, which consume most of the wet-process acid. Monoammonium phosphate and diammonium phosphate, two important examples of this type of fertilizer, are produced by ammoniating wet-process phosphoric acid with anhydrous ammonia. By adding various amounts of other ammonium salts, potash, and inert extenders, a great variety of solid and liquid fertilizers can be produced at any desired ratio of nitrogen-phosphorous-potassium content.

Because wet-process phosphoric acid contains a few impurities (such as fluoride) in significant amounts and many impurities in trace amounts, uses of wet-process acid in other fields are limited. If the overall economics are favorable, this acid can be used for uranium recovery[6] or for phosphate salt production. Phosphoric acid made from elemental phosphorus by the thermal process is used for foods and in applications requiring chemical purity. In 1966, thermal-process phosphoric acid accounted for only 22 percent of the total United States production of phosphoric acid, whereas wet-process phosphoric acid made up the balance.[1]

TRENDS IN WET-PROCESS PHOSPHORIC ACID MANUFACTURE

The current trend in wet-process phosphoric acid manufacture is toward larger producing units with closer control of operating variables. Two important incentives for change exist: the increasing demand for sulfuric acid has exerted strong upward pressure on sulfur prices, and handling and shipping costs have increased the demand for higher-strength phosphoric acid.

As the price of sulfuric acid increases, the relative cost of acidulation of phosphate rock with nitric acid will become more attractive. Nitric acid acidulation is presently practiced in Europe,[7] and an increase in the developmental activity on improvements in this process, and probably in methods for acidulation with hydrochloric acid, can be foreseen.

Special processes are used to concentrate 54 percent P_2O_5 to 70 percent P_2O_5 superphosphoric acid. The reduction in water content of course reduces shipping cost. This acid is less corrosive than 54 percent P_2O_5 acid. Because it can be supercooled without solidifying, it can be stored in liquid form at subfreezing temperatures. Further technological development is expected.

Another trend is toward processes that directly produce acid filtrates of higher P_2O_5 content. One designer offers a process that produces 42 percent P_2O_5 filtrate by a method involving two-stage crystallization.[9] Other designers are working on processes that achieve similar results. Solvent extraction is being investigated, and high acid concentrations have been achieved by solvent processes on a small scale.[10]

WET-PROCESS PHOSPHORIC ACID MANUFACTURE

PROCESS CHEMISTRY

The basic raw material of this process is phosphate rock, containing the mineral fluorapatite and numerous impurities. Fluorapatite, $Ca_{10}(PO_4)_6\ F_2$, is a salt from which phosphorus can be extracted as orthophosphoric acid by double decomposition with a mineral acid. In practice, 93 or 98 percent sulfuric acid is normally used. Calcium sulfate precipitates, and the liquid phosphoric acid is separated by filtration. The reaction is described by the following equation:

$$3\ Ca_{10}(PO_4)_6\ F_2 + 30\ H_2SO_4 + SiO_2 + 58\ H_2O \longrightarrow 30\ CaSO_4 \cdot 2H_2O + 18\ H_3PO_4 + H_2\ SiF_6$$

In commercial practice the sulfuric acid is generally mixed and diluted in the reaction vessel with a large excess of phosphoric acid in the rock slurry. By proper control of the temperature and amount of water in the slurry, crystal structure of the precipitated calcium sulfate can be controlled to facilitate filtration. Low temperatures and low acid content yield calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$, or gypsum, whereas higher temperature and higher acid strengths yield semi-hydrate, $CaSO_4 \cdot 1/2\ H_2O$, or anhydride, $CaSO_4$. The ease of filtration is dependent on proper growth, size, and shape of crystals. Most modern plants are designed so that they produce the dihydrate.

Phosphate rock usually contains 6.5 to 9.0 percent silica, which, in the presence of acid, reacts in various ways with the fluoride in the rock. It is probable that fluorine is released as a mixture of fluosilicic acid, silicon tetrafluoride, and hydrogen fluoride.

RAW MATERIALS

If phosphate rock ore were a simple calcium orthophosphate or even pure apatite, wet-process acid manufacture would be easier and cheaper than it is. Phosphate rock is found in workable amounts in many countries. The composition varies from one location to another and even within the same rock bed. The analysis in Table 2 of a high-grade Florida land pebble illustrates the normal complexity of phosphate rock. In addition to the constituents listed, other elements are usually present in traces.

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Table 2. COMPOSITION OF HIGH-GRADE FLORIDA LAND PEBBLE[10]

Component	Weight, %	Component	Weight, %
P_2O_5	35.5	F	4.0
CaO	48.8	Cl	0.01
MgO	0.04	CO_2	1.7
Al_2O_3	0.9	Organic carbon	0.3
Fe_2O_3	0.7	Na_2O	0.07
SiO_2	6.4	K_2O	0.09
SO_3	2.4	H_2O (100 °C)	1.8

Composition ranges of impurities for 15 types of phosphate rock from seven locations of origin are summarized in Table 3.

Table 3. IMPURITIES IN PHOSPHATE ROCK[11]

Component	Range of weight, %
MgO	0.01 - 2.2
Al_2O_3	0.5 - 15
SO_3	0.01 - 3
Cl	0.001 - 0.2
Na_2O	0.005 - 1.5
K_2O	0.1 - 1.0

Commercial phosphate rock usually contains 31 to 35.5 percent P_2O_5. Flourine content is usually in the 3.5 to 4 percent range. Because iron and aluminum oxides form insoluble phosphates, they are undesirable constituents. Carbonates are undesirable because they consume sulfuric acid, thus liberating carbon dioxide, which contributes to foaming. Some phosphate rock has a high organic content that may cause foaming and interfere with phase separations and the desired chemical reaction(s). For these reasons, each plant should be designed for the particular phosphate rock that it will use.

Although any strong mineral acid can be used to decompose phosphate rock, sulfuric acid is used for process and economic reasons. The insoluble calcium sulfate formed when sulfuric acid is used can be easily separated from the liquid. In order to make the strongest possible phosphoric acid and to decrease later evaporating costs, 93 or 98 percent sulfuric acid is normally used. Spent sulfuric acid can be used, but this introduces additional impurities that may contribute to foaming and increase corrosiveness. Any residual organic content of the spent acid may cause an odor problem.

FINAL PRODUCT

A modern, wet-process phosphoric acid plant produces 30 to 32 percent P_2O_5 acid which is then concentrated to about 54 percent. Table 4 shows a typical analysis of commercial wet-process phosphoric acid.

Table 4. COMPONENTS OF TYPICAL WET-PROCESS ACID[12]

Component	Weight, %	Component	Weight, %
P_2O_5	53.4	Na	0.2
Ca	0.1	K	0.01
Fe	1.2	F	0.9
Al	0.6	SO_3	1.5
Mg	0.3	SiO_2	0.1
Cr	0.01	C	0.2
V	0.02	solid	2.9
H_2O and other	37.56		

In addition to the components listed in Table 4, which may vary considerably, other trace elements are commonly present. Because commercial wet-process acid is a complex, corrosive material, corrosion is a major problem in its manufacture. The achievement of effective plant designs was not possible until modern construction materials were developed.

In addition to causing process difficulties, impurities affect physical properties of the acid. Commercial, wet-process acid has a higher viscosity than pure orthophosphoric acid of the same concentration. This tends to increase difficulty in filtering calcium sulfate formed during acidulation of the phosphate rock. In general, impurities indirectly affect atmospheric emissions by increasing corrosion and subsequent leakage, and increasing downtime, which provides opportunities for the escape of pollutants.

PROCESS DESCRIPTION

Most current process variations for producing wet-process phosphoric acid depend on decomposition of phosphate rock by sulfuric acid under conditions where gypsum ($CaSO_4 \cdot 2H_2O$) is precipitated. Several variants of this process are offered by various contractors. The Dorr-Oliver,[13] St. Gobain,[14] Prayon,[2] and Chemico[2] processes are among the better known. Most of the contractors in the chemical construction industry design and build these plants. Moreover, the growth of the fertilizer business has attracted some able new contractors during the past 5 years. In spite of the number of contractors in the field, new plants do not seem to differ fundamentally among themselves. In addition, several general trends are evident, such as the use of single-tank instead of multiple-tank reactors, one or two large horizontal tilting-pan filters, large plants of 1000-ton-per-day capacity and more, and closed systems where atmospheric emissions are minimized. Figure 1 is a flow diagram of a modern, wet-process phosphoric acid plant.

Finely-ground phosphate rock is metered accurately and continuously into the reactor, and sulfuric acid is added. Because the proper ratio of acid to rock must be maintained as closely as possible, these two feed streams use the best automatic control equipment available.

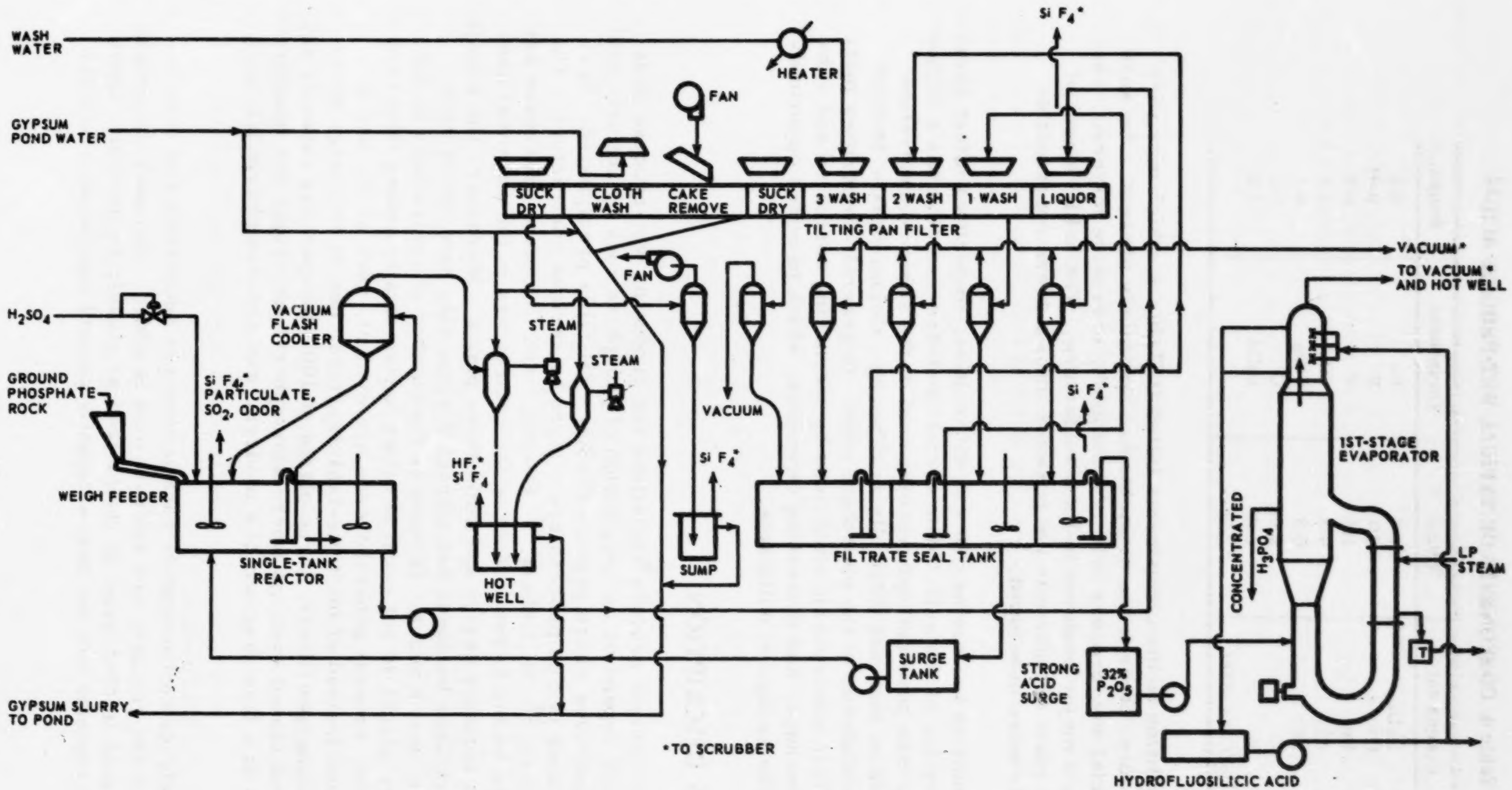
WASH WATER
HEATER
FAN
GYPSUM POND WATER
SUCK DRY
CLOTH WASH
CAKE REMOVE
SUCK DRY
3 WASH
2 WASH
1 WASH
LIQUOR
TILTING PAN FILTER
Si F$_4$*
VACUUM*
TO VACUUM * AND HOT WELL
FAN
H_2SO_4
VACUUM FLASH COOLER
STEAM
STEAM
GROUND PHOSPHATE ROCK
Si F$_4$* PARTICULATE, SO_2, ODOR
VACUUM
Si F$_4$*
1ST-STAGE EVAPORATOR
WEIGH FEEDER
HF,* Si F$_4$
Si F$_4$*
CONCENTRATED H_3PO_4
SINGLE-TANK REACTOR
HOT WELL
SUMP
FILTRATE SEAL TANK
LP STEAM
T
SURGE TANK
STRONG ACID SURGE
32% P_2O_5
GYPSUM SLURRY TO POND
*TO SCRUBBER
HYDROFLUOSILICIC ACID

Figure 1. Flow diagram illustrating wet-process phosphoric acid plant.

The single-tank reactor illustrated in Figure 1 is a circular, two-compartment system wherein reactants are added to the annular volume and the central volume is used for growing gypsum crystals. Some years ago, plants were built with several separate reaction tanks connected by launders, which are channels for slurry flow. The tendency now is to use a single tank with several compartments. In some of these designs, the slurry flows over and under a series of baffles.

Proper crystal growth depends on maintaining sulfate ion concentration within narrow limits at all points in the reaction slurry. The proper sulfate ion concentration appears to be slightly more than 1.5 percent. Lower levels give poor crystals that are difficult to filter; higher concentrations interfere with the reaction by causing deposition of calcium sulfate on unreacted rock.[14] Good reactor design will prevent sudden changes of sulfate ion concentration, will maintain this concentration and temperature near optimum, and will provide sufficiently long holdup time to allow growth of large, easily filterable crystals without the formation of excessive crystal nuclei. Impurities in small amounts often have a marked effect on crystal habit when they are present in a medium where crystallization is taking place. Usually this impurity effect is detrimental. Such impurities are likely to cause crystal fragmentation, small crystal size, or a shift to needles or other hard-to-filter forms. It is suspected that impurities in some plants and at some times interfere with desired crystal formation.

Concentrated sulfuric acid is usually fed to the reactor. If dilute acid is used, its water content must be evaporated later. The only other water entering the reactor comes from the filter-wash water. To minimize evaporation costs, it is important to use as little wash water as is consistent with practical H_3PO_4 recoveries.

Considerable heat of reaction is generated in the reactor and must be removed. This is done by blowing air over the hot slurry surface or by vacuum flash cooling part of the slurry and sending it back into the reactor. Modern plants use vacuum flash cooling. Figure 1 illustrates this method of cooling.

The reaction slurry is held in the reactor for periods up to 8 hours, depending on the rock and on reactor design, and is then sent to be filtered. The circular, horizontal, tilting-pan vacuum filter is illustrated in Figure 1. Older and smaller plants may use other types of filters.

In washing the resultant gypsum cake on the tilting-pan filter, wash-water flow is countercurrent to the rotation of the cake, and heated fresh water is used to wash the "cleanest" cake. These filters can be built in very large sizes, and designs are now approaching 1000-ton-per-day P_2O_5 capacity.

The 32 percent acid from the filter generally needs concentrating for further use. Current practice is to concentrate it by evaporation in two or three vacuum evaporators. Concentration to above 54 percent P_2O_5 is not practical, because the boiling point of the acid (Table D-1) rises sharply above this concentration, even at 27 inches Hg vacuum. Corrosion problems also become more difficult when concentration exceeds 54 percent. In the evaporator, illustrated in Figure 1, provision is made for recovery of fluoride as fluosilicic acid. This recovery feature is not necessary to the evaporation and its inclusion is a matter of economics. Many evaporation plants have not installed this device.

DISTRIBUTION OF FLUORINE

Figure 2 illustrates a typical material balance for fluorine originally present in phosphate rock. It should be noted that the results in any given plant may differ considerably from those shown in the figure, which represents an example based upon data from several sources. Actually, the fluorine distribution will depend upon the type of rock treated, process used, and kind of operation prevailing.

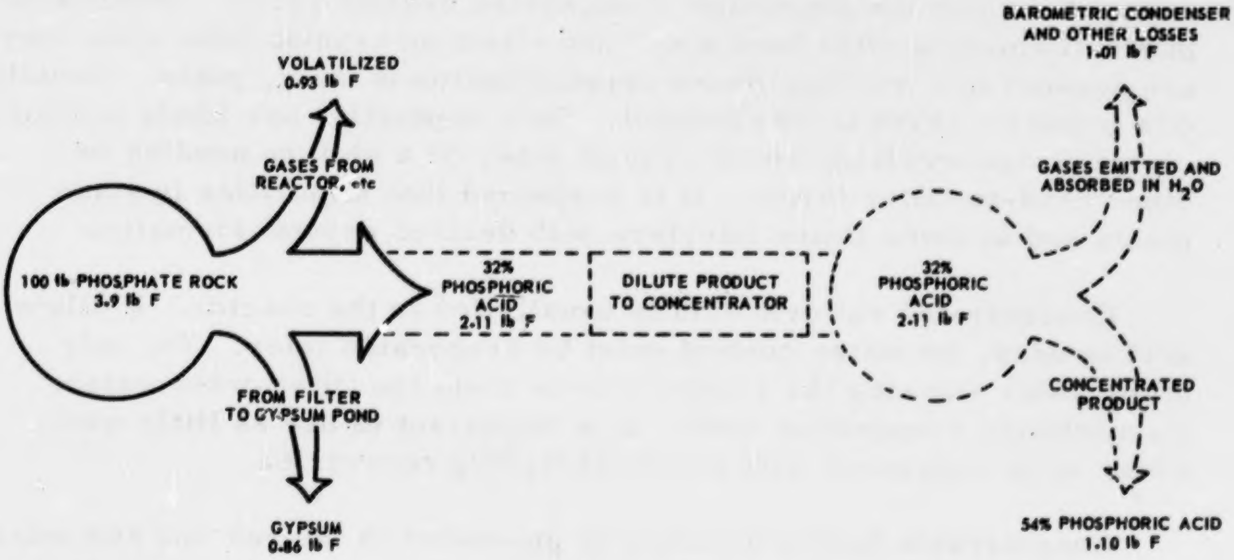
BAROMETRIC CONDENSER AND OTHER LOSSES 1.01 lb F
VOLATILIZED 0.93 lb F
GASES FROM REACTOR, etc
GASES EMITTED AND ABSORBED IN H_2O
100 lb PHOSPHATE ROCK 3.9 lb F
32% PHOSPHORIC ACID 2.11 lb F
DILUTE PRODUCT TO CONCENTRATOR
32% PHOSPHORIC ACID 2.11 lb F
FROM FILTER TO GYPSUM POND
CONCENTRATED PRODUCT
GYPSUM 0.86 lb F
54% PHOSPHORIC ACID 1.10 lb F

Figure 2. Typical material balance of fluorine in manufacture of wet-process phosphoric acid.

Figure 2 indicates that 0.93 pound of fluorine is volatilized (as HF, SiF_4, etc.) by acid attack on 100 pounds of the rock. This volatilization varies considerably in practice. If reactor slurry is cooled by air, the fluoride can be absorbed from the air stream by a water scrubber. If it is cooled by vacuum flash, much of the fluoride will be dissolved in the barometric-condenser water. This fluoride-bearing water may be sent to a pond, where limestone or lime may be added to raise the pH and convert fluoride to insoluble calcium fluoride. Here, silica would be present in the soil to convert hydrogen fluoride to fluosilicates.

The foregoing applies also to the concentration of the 32 percent acid, in which volatile fluorides also pass to the barometric condenser, which is part of the system used to create vacuum for the evaporator. Fluorides may be emitted from filters and seal boxes, feed boxes, and other points in the plant. The fluoride evolved from the acid-concentration step will be almost completely controlled if it is recovered, as illustrated in Figure 1, by conversion to hydrofluosilicic acid.

Figure 3 shows fluoride emissions from the water in an actual gypsum pond, as determined by personnel at plant 17. The experimental method used consisted in passing air, at a known rate, over a relatively large amount of gypsum-pond water and analyzing the exit air for fluoride. Measurements were made at six temperatures. The air-water interface was 20 feet long. It is doubtful that the air was saturated after this length of travel, so Figure 2 is probably conservative; this means that fluoride evolution from this particular pond, at the given windspeed and with reasonable vertical mixing of air above the pond, is probably somewhat greater than indicated by the curve.

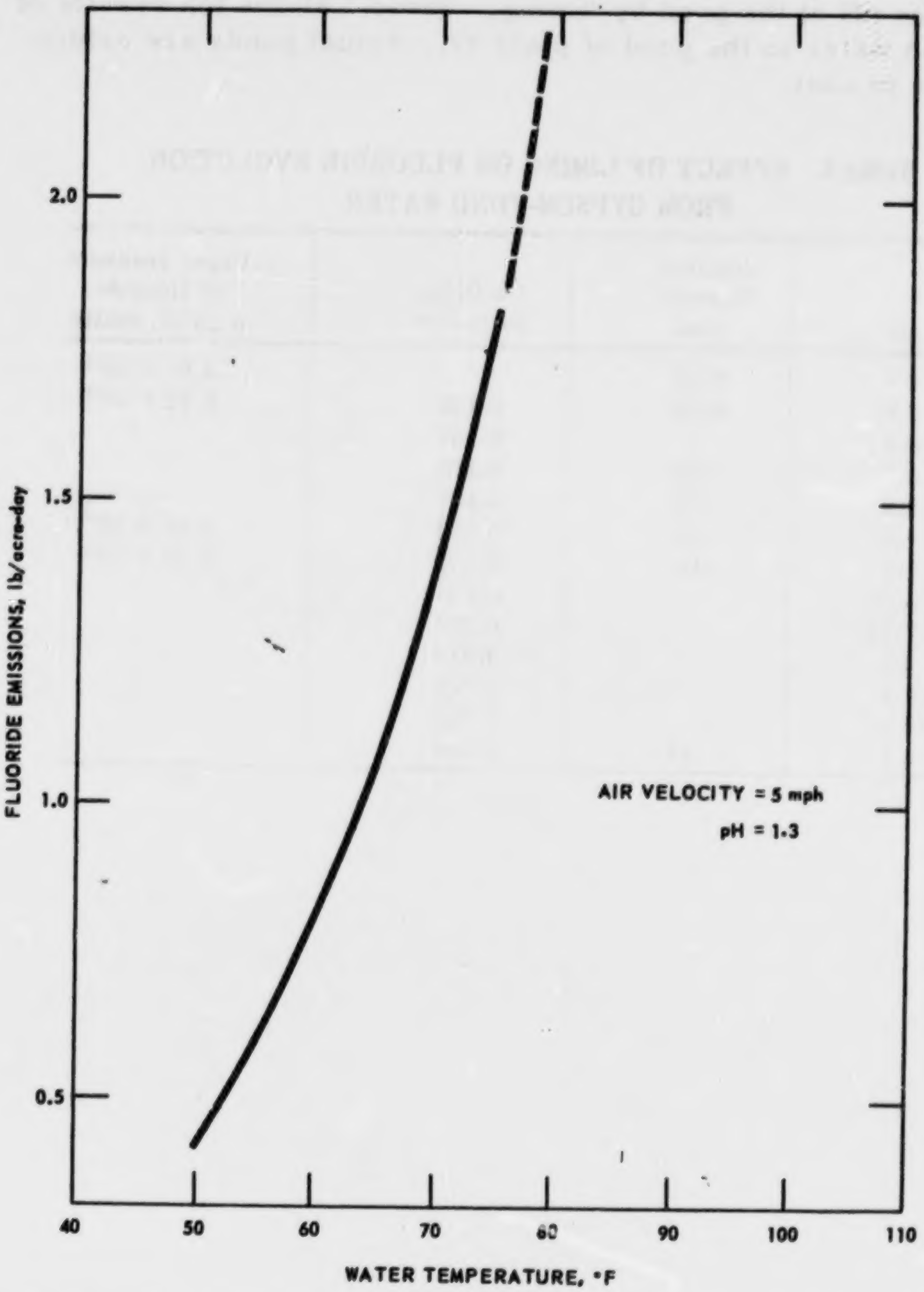

Figure 3. Fluoride emission from gypsum pond water containing 10,200 ppm fluorine.

The data in Figure 3 may be compared with those of a recent journal article (JAPCA 19(1): 15-17) where a gypsum-pond fluoride evolution of 0.16 pound per acre per day is given. In the author's opinion, this emission factor is a minimum. It is based on a plant other than plant 17; also the soluble fluoride concentration was about 4,000 parts per million and the pH was about 1.7.

Among the ten constituents analytically determined in plant 17 gypsum-pond water, were Na, K, Si, NH_4, and SO_4. This complexity of composition may cause the volatility of fluoride to differ among gypsum ponds, even at similar fluoride concentrations in the water and identical water temperatures.

Fluoride evolution from gypsum ponds may be made negligible by raising the pH of the pond by liming. Table 5 shows the results of liming the water in the pond of plant 17. Actual ponds are seldom limed due to cost.

Table 5. EFFECT OF LIMING ON FLUORIDE EVOLUTION FROM GYPSUM-POND WATER

pH	Soluble fluoride, ppm	$Ca(OH)_2$, lb/gallon	Vapor pressure of fluoride @ 25°C, mmHg
1.4	8125		13.8×10^{-6}
2.6	4000	0.116	6.22×10^{-6}
3.0		0.145	
3.3	450	0.156	
3.9	106	0.157	
4.5	100	0.160	0.86×10^{-6}
6.1	106	0.192	0.45×10^{-6}
6.25		0.193	
7.72		0.207	
9.7		0.213	
12.1		0.222	
12.3		0.246	
12.5	16	0.346	

EMISSIONS FROM WET-PROCESS PHOSPHORIC ACID MANUFACTURE

GENERAL INFORMATION

Emissions from wet-process phosphoric acid manufacture consist of rock dust, fluoride gases, particulate fluoride, and phosphoric acid mist, depending on the design and condition of the plant. Fluorine exists as various compounds in the collection equipment: as fluorides, silico fluorides, silicon tetrafluoride, and mixtures of the latter and hydrogen fluoride, the mol ratio of which changes in the vapor with the concentration of fluosilicate in the liquid and with temperature. Because of the complex chemistry, the composition of emissions is variable. The usual practice in sampling and analysis has been to avoid determinations of individual compounds such as silicon tetrafluoride and to express the various emissions as fluorine equivalents. Little information has been published on actual composition of emissions or on quantitative values of emissions from minor sources. Data available are mainly for emissions from digesters and filters, and are expressed as fluorine equivalents.

SOURCES OF EMISSIONS

Phosphate rock contains 3.5 to 4 percent fluorine, and the final distribution of this fluorine in wet-process acid manufacture varies widely. In general, part of the fluorine goes with the gypsum, part with the phosphoric acid product, and the rest is vaporized. The proportions and amounts going to gypsum and acid depend on the nature of the rock and on process conditions. Disposition of the volatilized fluorine depends on the design and operation of the plant. Substantial amounts pass off into the air unless effective scrubbers are used.

The reactor, where phosphate rock is decomposed by sulfuric acid, is the main source of atmospheric contaminants. The heat of reaction is considerable and must be removed to prevent an excessive temperature rise. A practicable way to remove heat is as latent heat of evaporation of the slurry water. The slurry is abrasive and highly corrosive to most materials of construction; therefore, for many years, cooling was accomplished by blowing air over the slurry surface, thereby removing latent heat with the water vapor evolved from the slurry and carrying away some additional heat as an increase in the sensible heat of the air. With better pumps and superior materials of construction, it became possible to vacuum flash cool the slurry by pumping it in and out of a vacuum vessel. Vacuum flash cooling is the most common method in current use. Emissions are minimized by this method because the system is closed. There is only a small volume of inert gases to be handled with the water vapor and fluorine. A disadvantage is that it is impractical to recover fluoride from the very large volumes of

barometric-condenser water used. Theoretically, it should be possible to remove this fluoride by the use of properly designed scrubbers ahead of the barometric condensers, but this is not normal practice at present.

Digester cooling by air blowing requires large volumes of air in relation to the water vapor and fluoride removed. The fluoride can be recovered by scrubbing; but because of the large volumes of gas handled, operating costs are increased substantially.

Acid concentration by evaporation provides another source of fluoride emissions. In this operation it has been estimated that 20 to 40 percent of the fluorine originally present in the rock vaporizes (Figure 2). The acid-concentration operation is usually vacuum evaporation, and the fluoride is partly dissolved in the barometric-condenser water. In acid concentration, good recovery of fluoride is possible by means of absorption of the vapors in water, forming hydrofluosilicic acid. A process has been patented[15] to scrub these vapors with a 15 to 25 percent hydrofluosilic solution at a temperature at which water vapor, which would dilute the solution, is not condensed. The water vapor itself is later condensed in the barometric condenser ahead of the vacuum system. The scrubbers are spray towers combined with vacuum evaporators to form single vessels, resulting in a series of evaporator-scrubbers. In such a vessel, vapors from the lower evaporator section pass to the spray chamber above, but the resulting fluosilicic acid flows to a storage sump; it cannot flow down into the vacuum evaporator. This arrangement is illustrated on the evaporator shown in Figure 1.

The filter is a third source of fluoride emissions. For circular filters, and for filters of the Georgini pan-filter type, most of the emissions are at feed and wash points. Emissions from filters are not large and can be controlled by the use of hoods, vents, and scrubbers.

In addition to these three main sources of emissions, there are many miscellaneous minor sources. These include vents from such sources as acid splitter boxes, sumps, and phosphoric acid tanks. Collectively, these sources of fluoride emissions are significant, and they are often enclosed and vented to a suitable scrubber.

Emissions from a wet-process phosphoric acid plant, except for rock dust, may come from: rock digesters, filters and their accessories such as the feed box and seal tank, the evaporator hot well, sumps, and acid vessels. In most plants, all of these sources are controlled.

Table 6 shows concentrations of fluoride at various points in the process ahead of control equipment. All units of emissions are grains of fluorine per standard cubic foot, except that total particulates are expressed in grains per standard cubic foot. These results were obtained from tests made by Public Health Service personnel.

Table 6. CONCENTRATION OF FLUORIDES FROM UNCONTROLLED PROCESS EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS

Gaseous fluoride		
From digester	0.014 - 0.41	
From filter	0.0021 - 0.0094	
From sump and vent	0.0035 - 0.024	
Particulate fluoride		
	Soluble	Insoluble
From filter	0.00065 - 0.00077	0.00002 - 0.00003
From digester	0.013 - 0.026	0.017 - 0.11
Total particulates		
From filter	about 0.017	
From digester	0.47 - 3.73	

Stack-test data show that greater quantities of fluorides are generated in digesters than in filters and sumps. Filter emissions of gaseous fluoride were in the range of 0.011 to 0.063 pound per ton of P_2O_5 produced; sump and vent emissions were as high as 0.26 pound per ton of P_2O_5; and emissions from digesters ranged from 0.037 to 2.16 pounds per ton of P_2O_5 made.

Total particulate emissions directly from process equipment were measured for one digester and for one filter, in different plants. As much as 11 pounds of particulates per ton of P_2O_5 was produced by the digester and approximately 0.20 pound per ton of P_2O_5 was released by the filter. Only 3 to 6 percent of these particulates were fluorides. Particulates can be removed by jet venturis and certain other types of wet collectors. If necessary, residual fluoride gases can be removed by scrubbers already mentioned.

High fluoride concentration and low pH of the scrubbing water will tend to evolve fluorides from the scrubber and from the gypsum pond, which stores the scrubbing water. Surveillance is advisable.

Small amounts of SO_2 are sometimes evolved from a digester; the origin of this gas is not clear. Odors sometimes develop from organic material in the phosphate rock or in the sulfuric acid used, if the latter is spent acid.

METHODS OF EMISSION CONTROL

CONTACTOR DESIGN CONSIDERATIONS

Reactions involved in phosphate rock attack by sulfuric acid are complex and subject to debate, but may be generally representated by the following equation:

$$3\ Ca_{10}(PO_4)_6\ F_2 + 30\ H_2SO_4 + SiO_2 + 58\ H_2O \longrightarrow$$

$$30\ Ca\ SO_4 \cdot 2\ H_2O + 18\ H_3PO_4 + H_2SiF_6,$$

Under the existing conditions of temperature and acidity, the fluosilicic acid decomposes as follows:

$$H_2\ SiF_6 \longrightarrow SiF_4 + 2HF$$

Actually, the mol ratio $\frac{HF}{SiF_4}$ changes with conditions, such as concentration, and is not usually equal to 2. The SiF_4 and HF constitute the gaseous emissions to be controlled. When SiF_4 contacts water, the following reaction occurs:

$$3\ SiF_4 + 4H_2O \longrightarrow 2\ H_2SiF_6 + Si\ (OH)_4$$

Hydrated silica in the wet and newly formed state sticks to control equipment surfaces and plugs gas flow channels. Furthermore, it absorbs additional SiF_4.

All wet-process phosphoric acid plants emit SiF_4 and probably HF to a lesser extent. Designers for control recognize this fact and send the various streams to scrubbers adapted to handle each stream. The tendency today is toward one scrubber combining the above functions and having at least two entrances to accommodate the different kinds of gases.

In general, control of HF by absorption is straightforward. Hydrogen fluoride can be absorbed by several kinds of scrubbers, including conventional packed towers and irrigated packed sections. Because of the tendency of SiF_4 to decompose and cause plugging due to the deposition of silica, high SiF_4 gas loadings are best reduced by spray towers or other devices that are less susceptible to plugging. After the SiF_4 loadings are substantially reduced, the residual SiF_4 can be handled without complications. A good design should include provision for removal of any silica that does form, especially if packing or grids are used.

CONTROL DEVICES

A control device should capture all of the emissions from processing without any leaks or losses. The device should then be able to

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absorb substantially all of the fluoride without equipment stoppage or failure due to plugup by solids, precipitated or otherwise. Ideally, the device should be inexpensive and the pressure drop and maintenance costs should be low. The following discussion covers control devices that are commonly used; not all of them are well adapted to general use in wet-process phosphoric acid plants. Most of them are adaptations of equipment pieces originally developed for use in other industries: such as, ordinary packed towers, which absorb some gases well, but which must be used with caution in wet-process phosphoric acid plants. A description of control equipment in the ten plants tested by Public Health Service personnel will be given later. Detailed information on emissions and the performance of emissions control systems is included in the Appendix, Tables A-1 through A-3. Tables 7, and 8 summarize these data.

Table 7. SUMMARY OF EMISSION DATA ON PERFORMANCE OF CONTROL EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS[a]

Plant number	1	2	3	4	5
Collector type	Rectangular spray chamber	Square horizontal spray duct	Venturi scrubber, water-actuated	Venturi scrubber, water-actuated	Spray cross-flow packed scrubber
Gaseous fluoride entering collector per ton of P_2O_5 produced, lb	1.265-2.16	Not determined	0.21-0.31	0.49-0.67	0.078-0.087
Gaseous fluoride emitted from collector per ton P_2O_5 produced, lb	0.52-0.63	0.072-0.101	0.027-0.047	0.028-0.038	0.006-0.018
Collection efficiency, %	57-72		84.2-87.0	92-96	80-92.4
Concentration of gaseous fluoride emitted from collector,					
grain/scf	0.075-0.090	0.0026-0.0035	0.0104-0.0147	0.018-0.023	0.0011-0.0032
ppm	202-243	7.0-9.4	28-40	49-62	3.0-8.6
Particulate emitted from collector per ton P_2O_5 produced, lb					
Total particulates	0.28-0.50	0.36-0.47	0-0.029		
Efficiency, %			98.5-100		
Insoluble particulate fluorides	0.0006-0.008	0-0.0013	none found		
Efficiency, %			100		
Soluble particulate fluorides	0.050-0.094	0.0075-0.036	0.0023-0.0029		
Efficiency, %			94.0-97.0		

[a] Plants 1-10 were tested by NAPCA.

Table 7 (continued). SUMMARY OF EMISSION DATA ON PERFORMANCE OF CONTROL EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS[a]

Plant number	6	7	8	9	10
Collector type	Two impingement scrubbers in series	Spray cross-flow packed scrubber	Spray cross-flow packed scrubber	Cyclone spray tower	Spray cross-flow packed scrubber
Gaseous fluoride entering collector per ton of P_2O_5 produced, lb	0.013-0.016	1.20-1.48	0.05-0.06	0.85-1.00	Not determined
Gaseous fluoride emitted from collector per ton P_2O_5 produced, lb	0.006-0.011	0.10-0.17	0.0170-0.022	0.047-0.082	0.135-0.157
Collection efficiency, %	15-62	86-93	56.7-68.4	90.4-95.3	
Concentration of gaseous fluoride emitted from collector,					
grain/scf	0.0020-0.0037	0.0054-0.0088	0.0022-0.0029	0.0016-0.0029	0.0120-0.014
ppm	5.4-10.0	15-24	5.9-7.8	4.3-7.8	32-38
Particulate emitted from collector per ton P_2O_5 produced, lb					
Total particulates					0.29-0.36
Efficiency, %					
Insoluble particulate fluorides					0.006-0.09
Efficiency, %					
Soluble particulate fluorides					0.070-0.14
Efficiency, %					

[a] Plants 1-10 were tested by NAPCA.

Table 8. SUMMARY OF EMISSION DATA ON PERFORMANCE OF CONTROL EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS[a]

Plant number	11	12	13	14
Collector type	Venturi scrubber, water-actuated	Cyclonic spray	Spray cross-flow packed scrubber	Spray cross-flow packed scrubber
Gaseous and water-soluble particulate fluoride entering collector per ton of P_2O_5 produced, lb	2.0	7.6	0.53	77
Gaseous and water-soluble particulate fluoride emitted from collector per ton of P_2O_5 produced, lb	0.26	1.23	0.044	0.038
Efficiency, %	87	84	92	99.9
Concentration of gaseous and water-soluble particulate fluoride emitted from collector,				
grain/scf	0.058	0.031	0.0032	0.0019
ppm	167	87	9	5

[a] Information on plants 11 through 13 acquired through private communication.

Table 8 (continued). SUMMARY OF EMISSION DATA ON PERFORMANCE OF CONTROL EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS[a]

Plant number	15	16
Collector type	Impingement	Packed tower, two-stage cyclonic scrubber, in parallel
Total fluoride emitted from collector per ton of P_2O_5 produced, lb	0.037	0.0073
Concentration of total fluoride emitted from collector,		
grain/scf	0.0087	0.00035
ppm	24	1

[a] Information on plants 15 and 16 acquired through questionnaire.

SPRAY CROSS-FLOW PACKED SCRUBBER

Figure 4 illustrates a spray cross-flow packed scrubber. In theory[18] and in practice, the spray cross-flow packed scrubber is the most satisfactory control device presently available for general use in wet-process phosphoric acid manufacture, and many new plants and capital replacements employ this scrubbing principle. This type of scrubber is used in plants 5, 7, 8, and 10 summarized in Table 7, and described in the section, "Description of Control Equipment in Plants Tested by Public Health Service." The gas streams of a particular plant can be treated in the spray cross-flow packed scrubber. Those gas streams that precipitate solids go into the spray section, and streams containing mostly hydrogen fluoride go to the packed section, as does all gas leaving the spray section. The packed section is seldom more than 3 or 4 feet thick and it is usually set up on edge, with gas passing through it horizontally. Wash water is poured over the top of the packing and runs down at right angles to the motion of the gas.

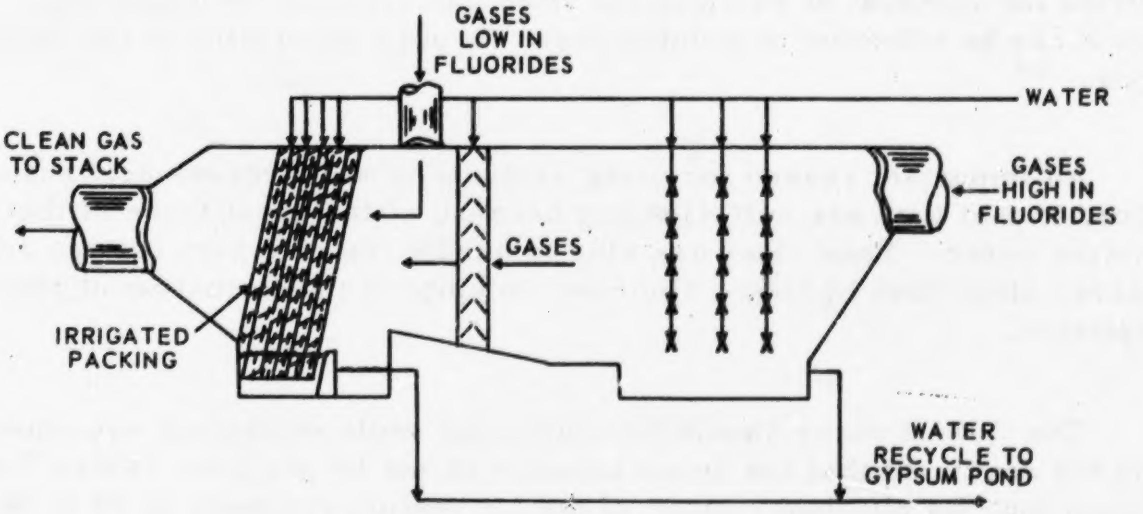

Figure 4. Principle of the spray cross-flow packed scrubber.

This tends to wash away any solids that escape precipitation in the empty spray section of the device and settle on the packing. The packing itself is usually a light polyethylene structure having many liquid redistribution points and causing only low pressure drop. Plant-test results show a 1- to 8-inch water-pressure drop. It is possible to irrigate the packing with a high water rate for the first few inches after the entrance of the gas into the packing to wash away particulates and precipitates.

Because of its design, this collector tends to operate free from plugging, and high degrees of fluoride removal can be achieved by its use. If necessary, the packing can be easily washed or replaced. Table 8 indicates relatively high performance for this type of collector, showing that gaseous fluoride emissions from the collector are in the range of 0.001 to 0.014 grains per standard cubic foot and collector efficiency is 57 to 99.9 percent. It should be noted, however, that the 99.9 percent collection efficiency was obtained for an extremely high inlet fluoride loading (i.e., 3.9 grains per standard cubic foot of gas).

PACKED TOWER

This device can be designed for any degree of hydrogen fluoride removal; unfortunately, it is subject to plugging due to precipitation from some compounds of fluorine, such as the solid reaction products of SiF_4 and water. Development of self-cleaning packing has not yet been achieved. Plant 16, as shown in Table A-3, had a 5-pound-per-day fluoride emission rate from this type of scrubber. This datum illustrates that good scrubbing can sometimes be accomplished with a packed tower.

VENTURI SCRUBBER

For economic reasons, the manufacturers of wet-process phosphoric acid prefer the water-actuated venturi or jet venturi scrubber rather than the gas-actuated type. The jet venturi is primarily a device for removal of particulates from gas streams by impaction, yet it can be effective on soluble gases through absorption in the motive water.[19]

An important reason for using venturis in wet-process acid service, is that they are self-cleaning because of the great force of the motive water. Thus, they are able to handle fluoride particulates and gases, other than hydrogen fluoride, in spite of the formation of precipitates.

The flow of water should be continuous while emissions are entering the device so that the spray nozzle will not be plugged. Tables 7 and 8 shows that the efficiency range of the jet venturi scrubber is 84 to 96 percent. Gaseous fluoride emissions from this scrubber are in the range of 0.0104 to 0.023 grain per standard cubic foot.

SPRAY TOWER

Spray towers are relatively inexpensive to build and are not a source of much trouble from plugging, if the sprays are carefully designed. Towers, however, do not usually have enough transfer units to remove fluorine effectively. The performance of cyclonic spray towers (one of several types of spray towers), is indicated by data presented for plants 9 and 12, in Tables 7 and 8. Collection efficiencies of this device for gaseous fluorides range from 90 to 95 percent. Emissions of gaseous fluorides from plant 9 are in the range of 0.0016 to 0.0029 grain per standard cubic foot. The overall removal efficiency of this device for gaseous and water-soluble particulate fluorides for plant 12 was 84 percent. The concentration of fluoride emission was 0.031 grain per standard cubic foot.

Some devices that are not true spray towers were tested, (as reported for plants 1 and 2, in Table A-1). These are rather crude devices that have mediocre performance resulting from bypassing, defective water distribution, poor spray drop size, and other factors. Particulate removal was notably poor in these devices. Efficiency of gaseous fluoride removal was 57 to 72 percent for the one tower where both inlet and outlet could be sampled, and the range of gaseous fluoride emissions was 0.075 to 0.090 grain per standard cubic foot.

IMPINGEMENT SCRUBBER

There are several types of scrubbers in this classification, but the impingement type most commonly used in the fertilizer industry is the Doyle Scrubber. Results of operating a scrubber of this type are reported for plant 6 in Table 7.

Gas to be treated contacts the surface of a pool of water at high velocity, undergoing a reversal in direction. Solids impinge on the water and are retained, and absorption of fluoride gases is promoted by the turbulence and by the droplets generated by impact.

Theoretically, one would not expect high absorption efficiency for gases in this scrubber; however, a better efficiency range than the 15 to 62 percent range indicated for plant 6 should normally be possible. This particularly poor efficiency was probably due to the abnormally low inlet fluoride concentrations during these runs. In addition, this scrubber normally serves a nearby triple-superphosphate plant and this connection was blanked off during the stack tests of the acid plant. The resulting gas flow was substantially below design, which would be expected to contribute to low efficiency.

PERFORMANCE OF CONTROL SYSTEMS

Ten plants were sampled by Public Health Service personnel and the gases were analyzed for gaseous fluoride. In a few cases, concentrations of particulates were also determined. Tables A-1 and A-2 summarize the control-equipment performances calculated and the operating data taken. Control-equipment efficiencies have been determined wherever sampling of both inlet and outlet gases was possible.

Tables 7 and 8 have been developed from the primary data in Tables A-1, A-2, and A-3, and summarize the performance of the collectors used. The Public Health Service tests were mainly concerned with collector performance and the efficiency of fluoride removal. For a more detailed description of the fluoride scrubbers tested, refer to the section entitled "Description of Control Equipment in Plants Tested by Public Health Service."

The more efficient types of scrubbers are represented in Table 7 by those installed in plants 3 through 10. Particulates are reported only for plants 1, 2, 3, and 10 because so little particulate matter was found that testing for it was discontinued. For example, the venturi scrubber in plant 3 is a highly efficient type and chemical analysis of various samples of the exit gas from this scrubber varied from no detectable particulates to 0.029 pound per ton of P_2O_5 produced, or about 0.009 grain per standard cubic foot (Table A-1). Analyses of scrubber exit gases in plants 4 through 9 gave similar negligible values in every case sampled. A few of these scrubbers were not adapted to particulate sampling, because isokinetic sampling was made impossible by equipment geometry and piping arrangement. Therefore, no particulate fluoride results can be given for plants 4 through 9. Because plant 10 showed 40 percent opacity of the stack plume, read at time of the sampling, particulate samples were taken from the stack. Table 7 verifies the visual evidence given by the stack-plume opacity by showing a range of 0.29 to 0.36 pound of total particulates in the plume per ton P_2O_5 produced, or a concentration of 0.025 to 0.031 grain per standard cubic foot.

Data in Table 7 show a large variation in insoluble particulate fluorides, in the range of 0 to 0.09 pound of fluoride per ton of P_2O_5 produced. This is because the analytical chemical methods determine total particulate fluoride and soluble particulate fluoride directly; insoluble particulate fluoride is then calculated by difference. Because minuend and subtrahend happen to be nearly equal, subtraction gives a small result and the variation shown for insoluble particulate fluoride values is due to small differences between two relatively large numbers.

In plant 3, the weak phosphoric acid from the digester is concentrated by direct contact evaporation or submerged combustion using hot combustion gases produced by burning hydrocarbon off-gases. The concentrator off-gases are fed through a spray chamber, two impingement scrubbers in series, two venturi fume scrubbers in series, and a cyclonic spray scrubber before being discharged into the stack. None of these control devices are noted in the tables. Originally, only the spray chamber and venturi scrubbers were installed, but these had so little effect on the acid fog formed in the concentrator that the other items were added. In spite of the presence of these several evaporator emission abatement scrubbers, company stack tests reported emissions of 250 pounds of P_2O_5 per day and 1400 pounds of fluoride per day. Even assuming reasonable sampling and analytical errors, it seems clear that direct contact-combustion-gas evaporation of phosphoric acid produces stubborn fogs that pass through most scrubbing equipment essentially unaltered. This is one of the reasons that such evaporation systems are seldom built today. Instead, closed vacuum evaporators in two or more stages are commonly used to concentrate phosphoric acid. The Public Health Service stack-gas tests made at plant 3 were done at the digester-off-gas scrubber, and not at the evaporator stack.

At plant 6, concentration of fluoride in the inlet gases was low (about 0.005 grain per standard cubic foot) making the scrubber appear inefficient. The same comment applies to plant 8; the type of scrubber used in this plant can achieve efficiencies of over 99 percent.[16]

Concentrations of emissions from various types of scrubbers in the ten plants tested are given in Table 7 and Appendix Tables A-1, and A-2. Particulate emissions from scrubbers were 0.0 to 0.50 pound per ton of P_2O_5 produced. Gaseous fluoride emissions from most of these ten plants were in the range of 0.006 to 0.17 pound per ton of P_2O_5 produced.

Sulfur dioxide was detected in gases from the reactor, and from filters, and vents of plant 7. Three analyses were made of the stack gas after scrubbing and a concentration of about 13 parts per million was found. For plant 8, stack concentrations were 6 to 18 parts per million and for plant 9 the range of stack concentrations was 1 to 2 parts per million. These correspond to average SO_2 emissions of 87 and 6 pounds per day for plants 8 and 9, respectively. The origin of this sulfur dioxide is not clear; perhaps it comes from reduction of the sulfuric acid by organic material of the phosphate rock, or even from dissolved SO_2 in the sulfuric acid itself.

Table A-3 gives some fluoride-scrubber performance data from additional sources. Information for plants 11 through 14 was obtained through private communication. Plants 13 and 14 indicate the degree to which the rate of untreated emissions depends on processing. Thus, plants 13 and 14 use different processes and generate respectively 240 and 34,600 pounds per day of particulate fluorides to send to their scrubbers. Also, they show again that high scrubber efficiency is more likely to be obtained if the inlet fluoride concentration is high. Both scrubbers were designed to reduce the fluoride emissions to 0.01 ton per day. They have been quite successful in meeting design specifications, as have several other designs of this type.

Data for plants 15 and 16 were obtained in response to a questionnaire. Reported concentrations were determined by sampling and analysis by plant staffs.

Plant 15 was sampled downstream from the scrubbers. Fluoride analyses were by the Willard and Winter method. Circular, horizontal, tilting-pan filters are used in this plant. Samples from the filter were taken using an experimental hood over the slurry charge area on one filter and extrapolating data to the total plant filter area. A baghouse is used to control rock dust to a design value of 0.002 grain per standard cubic foot but no measurements are available on performance.

Plant 16 has two trains: one served by a cyclonic scrubber, and one by a packed tower. The tilting-pan filter is hooded and vented to the system served by the cyclonic scrubber and both scrubbers are vented to a common 120-foot stack from which the gas samples were taken. The stack was sampled at the top and the modified Willard and Winter distillation method was used to determine fluorine content.

Table A-4 is derived from a paper by Huffstutler and Starnes.[17] Certain of their data are presented, but differences between plant capacity and production rate at times of their tests are not stated. The given emission values, in pounds per hour, are based on tests by the Florida State Board of Health and by the companies or their consulting firms. Company samples and those of the State Board were not taken at the same time.

The emission rates presented in Table A-4 agree reasonably well in magnitude with the results of plants tested in this MCA-PHS study, summarized in Table 7. Actually, many of the control units that were measured to make Table A-4 have been improved or replaced, and current emissions from the same plants probably now contain less fluorine.

DESCRIPTION OF CONTROL EQUIPMENT IN PLANTS TESTED BY PUBLIC HEALTH SERVICE

Plant No. 1 - The digester collector used in this plant is a water-spray chamber 4 feet long, 3 feet wide, and 5 feet high. A center baffle extends from the top to within 6 inches of the bottom of the chamber. Gases enter the top of the first compartment, pass under the baffle and exit through the side of the second compartment. Water sprays are provided on 3 sides of the inlet compartment and on top of the discharge compartment. The filters have a hood which collects vapors and discharges them to the atmosphere through the roof of the building.

Plant No. 2 - The collector used here treats fluoride-containing gases from the digesters. The collector itself is a duct, 100 feet long and 4 feet square. Gases enter this duct at several points from 3 of 4 digesters. Eight 3/4-inch water-spray nozzles are provided in the top of the collector duct and five in the sides. Water-flow rate could not be determined.

Plant No. 3 - The off-gases from two digesters pass to a water-actuated venturi scrubber and then to the stack. The scrubber discharge chamber is 6 feet - 6 inches in diameter and 6 feet in height. The venturi scrubber is actuated by a pump rated at 400 gallons per minute, 46 pounds per square inch gauge, and 25 horsepower. This plant uses only spent acid for digesting the phosphate rock.

Plant No. 4 - This plant is a one-reactor, Prayon unit. Gases from the digester pass to a water-actuated venturi scrubber. This discharges to a closed tank, then to a stack via a fan rated at approximately 1,600 cubic feet per minute. The weak-acid holding tank is also vented to the duct leading to the scrubber. The collector is a 3-foot-by-14-foot venturi eductor scrubber, designed for a pressure drop of 2.35 inches of water at a water rate of 475 gallons per minute at 90 pounds per square inch gauge.

Plant No. 5 - The fluoride scrubber is a spray cross-flow, packed unit 9 feet wide, 10 feet high, and 30 feet long. There are three chambers of sprays with wood baffling and a 7-foot-10-inch section of polyethylene ring packing. Gases from the digesters enter the spray section through a 30-inch plastic duct. Gases also enter the packed section separately, from the filter, filter feed box, filter flash column seal tank, filter seal pump, the 22-percent-acid feed box, and the sump. These are combined for entry through a 26-inch diameter duct. Design water rate is 1000 gallons per minute for a gas pressure drop of 5.8 inches of water at 380 feet per minute superficial gas velocity. The blower is rated at 40,000 cubic feet per minute and the stack has an inside diameter of 4 feet.

Plant No. 6 - There are two reaction lines. Discharge from each reactor is fed to the scrubbing system by a 26-inch diameter duct. The scrubbing system consists of two impingement scrubbers in series. Each scrubber is 10-1/2 feet wide, 13 feet long, and 12 feet high. Pressure drop averages about 9 inches of water for the first scrubber and 7 inches of water for the second. Effluent from the scrubber passes to a stack 4 feet 2 inches in diameter.

The above scrubbers also serve part of a nearby triple-superphosphate plant. This connection was closed off during the test and sampling program.

Plant No. 7 - Fluoride-containing gases are collected in a spray cross-flow, packed scrubber 9 feet wide, 9 feet high, and 42 feet long. The packed section contains 3 feet of polyethylene rings. Pond water is recirculated to the scrubber at a rate of about 800 gallons per minute at 60 pounds per square inch gauge. Gases are collected from digesters, filters, and sump tanks.

Plant No. 8 - Fluoride emissions are collected from the digesters and from the filter. The collector is a spray cross-flow, packed scrubber, 10 feet high, 11 feet wide, and 33 feet 7 inches long. The packed section contains 6 feet of polyethylene rings. About 1000 gallons per minute of pond water is recirculated at about 70 pounds per square inch gauge. Pressure drop through the scrubber is approximately 8 inches of water for a gas flow of approximately 40,000 cubic feet per minute at a superficial velocity of 360 feet per minute.

Plant No. 9 - Gases from the digesters, filter, evaporator hot well, clarification tanks, and 54-percent-acid storage tank are sent to a spray tower scrubber that is 40 feet tall and has an inside diameter of 10 feet. The gas enters the top of the tower tangentially, passes downward past three banks of water spray nozzles, and then through about 8 inches of polyethylene packing at the tower bottom, to agglomerate small drops of water. The scrubber pressure drop is about 8 inches of water at a pond-water recirculation rate of 900 gallons per minute at 60 pounds per square inch gauge. Gas rate is around 30,000 standard cubic feet per minute and the exhaust stack from scrubber is 33 inches in diameter. Gas leaving the bottom of the scrubber passes tangentially into the base of the stack where some additional drops of water are removed.

Plant No. 10 - This collector is a spray cross-flow, packed scrubber, 6 feet wide, 7 feet high, and 31 feet long. Gases from the digester are fed to the spray section and combined emissions from filter feed tank, filter, and 22-percent-acid mixing box go to the packed section. A third line vents the sump tank, vacuum-scrubber seal tank, hot well, and filter seal tank indirectly to the filter. There is approximately 174 cubic feet of polyethylene-ring packing and the scrubber pressure drop is somewhat greater than 1 inch of water at a water rate of 420 gallons per minute and superficial gas velocity of 280 feet per minute.

Because of the tight piping arrangement, isokinetic sampling before the scrubber was impossible and tests and samples were run only on the 30-inch-diameter, scrubber-outlet stack.

HANDLING OF SCRUBBER WATER

New plants can be designed to control fluoride emissions by incorporating closed process procedures where possible and by scrubbing the gas streams from those points where emissions occur. Because effective scrubbing of the large volumes of gas usually involved requires substantial quantities of water, it is common practice to use a large storage pond from which water is recycled to the scrubbers. Washed gypsum from the filters is also sent to this pond. Residual phosphoric acid in the gypsum slurry tends to reduce the pH, as does hydrogen fluoride, (including that produced by the decomposition of silicon tetrafluoride) picked up by the scrubbers. While a low pH can be expected to increase the vapor pressure of hydrogen fluoride, thereby promoting the release of this gas to the atmosphere, this tendency is opposed by the presence of soluble calcium in the gypsum pond which will react with the fluoride to form the highly insoluble calcium fluoride. Because calcium sulfate is many times more soluble than calcium fluoride and becomes even more soluble as the pH is lowered, there is always an excess of soluble calcium in the gypsum pond. The vapor pressure of residual hydrogen fluoride can be further reduced by raising pH, for example, by adding hydrated lime or limestone, however, this procedure is not generally practiced in the wet-process acid industry.

CURRENT AND FUTURE AIR POLLUTION POTENTIAL

Over 400,000 tons of fluorine was present in the phosphate rock consumed in making wet-process acid in 1966. Theoretically, the wet-process acid production of 1966 could have released about 200,000 tons of fluoride into the atmosphere of the United States. Actually, because of the extensive use of scrubbers, the amount released was substantially smaller.

Much attention is now being given to closed designs, better collection systems, and improved mass-transfer design, both for existing plants and for new construction. Emission sources varying greatly in fluoride concentration are treated by different scrubbers: dilute fluoride concentrations are sent to scrubbers with low liquid concentrations and large numbers of transfer units; higher fluoride concentrations are sent to scrubbers with high liquid concentrations and one or two transfer units.

SUMMARY OF SAMPLING AND ANALYTICAL TECHNIQUES

Stack-sampling and analytical work for the joint MCA-PHS study of wet-process phosphoric acid manufacture was done by the Public Health Service field test team with Public Health Service laboratory support. Detailed descriptions of these sampling and analytical techniques are presented in Appendix B.

PARTICULATE FLUORIDES

Particulate matter, as collected by the Public Health Service sampling train, includes any materials that are solid or liquid at 250°F. This temperature level is necessary to cause complete reaction between the hydrogen fluoride in the sample and the silicon dioxide in the glass probe. It should be noted that particulate matter also includes any residue left from liquid evaporated at this temperature. Soluble fluoride particulate matter is that part of the total particulate matter collected that will dissolve in water. Total particulate fluoride is determined by acidifying the sample and then distilling the slurry. The amount of insoluble particulate fluoride is the difference between total and soluble particulate matter.

At each point sampled for particulate fluoride, pitot tube traverses were made to determine the velocity profile of the gases in the duct. Sampling was performed isokinetically at a number of traverse points. The stack gases were drawn through a sampling train consisting of a glass probe, cyclone, and glass-fiber filter collection system, heated to preclude condensation from the sample gas stream and enhance the reaction of the fluoride gas with the glass. The cyclone collected particles larger than 5 microns. Particles smaller than 5 microns were collected on the fine, glass-fiber filter. Particulate fluoride analysis was done by the Spadns Determination of fluorides.

GASEOUS FLUORIDES

Gaseous fluorides were collected in two different ways. The first method uses the particulate-matter train as described above, plus four Greenburg-Smith impingers in an ice bath. Deionized water is used in the impingers to collect the gas sample. This gas sample will contain any fluorides driven off by evaporation in the heated portion of this train.

Gas samples were also collected nonisokinetically in a gas train. This is a much simpler train than the one previously described. A measured gas volume is pulled through a heated glass probe, a heated pressure filtration funnel, and then through four midget impingers using deionized water as the absorbing agent. The midget impingers

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are used because the sensitivity of the analytical method requires only a small sample. Gaseous fluorides were also analyzed by the Spadns Determination of fluorides.

GLOSSARY OF TERMS

°Be	Degrees Baumé (unit of specific gravity)
°C	Degrees centigrade
cfm	Cubic feet per minute
ΔP	Pressure drop
ft	Feet
°F	Degrees Fahrenheit
fpm	Feet per minute
gpm	Gallons per minute
gr	1 grain (7,000 grains = 1 pound)
HP	Horsepower
ID	Inside diameter
lb	Pound
ppm	Parts per million
psia	Pounds per square inch absolute
scf	Standard cubic feet measured
scfm	Standard cubic feet per minute, 60° F and 29.92 inches Hg
T	Short ton (2,000 pounds)

CHEMICAL SYMBOLS

Al	Aluminum
Al_2O_3	Aluminum oxide
C	Carbon
Ca	Calcium
CaO	Calcium oxide
$Ca_{10}(PO_4)_6F_2$	Apatite (Fluorapatite)
$CaSO_4$	Calcium sulfate, anhydrous
$CaSO_4 \cdot 1/2\ H_2O$	Calcium sulfate, semi-hydrate
$CaSO_4 \cdot 2H_2O$	Calcium sulfate, dihydrate, gypsum
Cl	Chlorine
CO_2	Carbon dioxide
Cr	Chromium
F	Fluorine
Fe	Iron
Fe_2O_3	Iron oxide, ferric oxide
HF	Hydrogen fluoride
H_2O	Water
H_2SO_4	Sulfuric acid
H_2SiF_6	Hydrofluosilicic acid
H_3PO_4	Orthophosphoric acid
K_2O	Potassium oxide
K_2SiF_6	Potassium fluosilicate
Mg	Magnesium
MgO	Magnesium oxide
Na	Sodium
Na_2O	Sodium oxide
$NaOH$	Sodium hydroxide
Na_2SiF_6	Sodium fluosilicate
P_2O_5	Phosphorous pentoxide
SiF_4	Silicon tetrafluoride
$Si(OH)_4$	Hydrated silica
SiO_2	Silica or silicon dioxide
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide

DEFINITIONS

Air contaminant	**Dust, fumes, gas, mist, smoke, vapor, odor, or particulate matter or any combination thereof present in the atmosphere.**
Apatite	**$Ca_{10}(PO_4)_6 F_2$ - The main phosphorous bearing component of phosphate rock.**
Attack tank	**See reactor.**
Barometric condenser	**Device used to condense steam from vacuum jet. . Uses direct contact of steam with cold water and 34 foot water leg to balance atmospheric pressure and allow water to escape by gravity.**
Centistokes	**Centipoise/specific gravity (Table D-2).**
Collector	**See control device.**
Control device	**One or more pieces of process equipment used to remove air pollutants from gas stream.**
Crystal nuclei	**Small crystals in a reactor, which furnish sites on which additional material of the same kind can deposit. See reactor.**
DAP	**Diammonium phosphate, made by reacting anhydrous ammonia with wet-process phosphoric acid.**
Digester	**See reactor.**
Effluent	**Waste-gas stream that enters the atmosphere from the process.**
Emission	**Any gas stream emitted to the atmosphere.**
Evaporator	**Unit which concentrates 32 percent P_2O_5 acid, by vacuum evaporation, submerged combustion or otherwise.**
Filter	**Device to remove calcium sulfate from dilute phosphoric acid by forcing the slurry through a cloth or screen.**

Fluorapatite	**See apatite.**
Fluorine	**Generic term referring to fluorine content of any material in a wet-process phosphoric plant.**
Fog	**Small liquid particles which form relatively stable aerosols and are notoriously difficult to collect. Typical size range, 1 to 100 microns.**
Gypsum	**Common name for $CaSO_4 \cdot 2H_2O$, calcium sulfate dihydrate.**
Gypsum pond	**A large pond, commonly unlined, and used to dispose of gypsum from the wet-process phosphoric acid filters. The pond also acts as a surge for fluoride scrubber water, which is commonly recycled to the scrubbers.**
Impingement scrubber	**A device which impinges a gas at high velocity onto a liquid surface, followed by a 180° reversal on exit, such as the Doyle scrubber.**
Launder	**A channel, usually rectangular, for gravity conveying slurry from one reactor to another.**
NSP	**Normal superphosphate, made by reacting phosphate rock with concentrated sulfuric acid. NSP contains about 20 percent P_2O_5.**
P_2O_5, 32 percent	**The usual product of the filter in a wet-process phosphoric acid plant. This concentration limit is set by the process used and by economics.**
P_2O_5, 54 percent	**The normal limit of concentration by evaporation of 32% P_2O_5. Set by boiling point elevation and economics. See superphosphoric acid.**
Phosphate rock	**The only commercial ore of phosphorus, widely distributed over the world and containing many trace impurities. See apatite.**
Phosphoric acid	**H_3PO_4, orthophosphoric acid, the main phosphorus bearing component of wet-process acid.**

Reactor	**One or more tanks or vessels in which the reaction between phosphate rock and sulfuric acid is carried out to make wet-process phosphoric acid.**
Scrubber	Generic term for any device in which contaminants are removed from a gas by contacting with an absorbing liquid, usually water or solutions of base or acid.
Spent acid	Sulfuric acid which has been used for another purpose, but is still reasonably high in concentration such as, used nitration acid.
Spray tower	A scrubber for contacting gas with a spray of water inside a tower. May have straight line motion or tangential motion.
Spray cross-flow packed scrubber	A scrubber providing two or more sections to treat plant gas streams according to their composition. See description of control equipment, for plants 5, 7, 8, 10, and Fig. 4.
Stack test	Sampling and analysis of any gaseous effluent which may also contain particulates.
Submerged combustion	Actual contact of flame with liquid by total submergence of the burner. Used in concentration of wet-process phosphoric acid, but not common.
Superficial gas velocity	Gas velocity in an equipment piece (such as a packed tower) calculated as if the equipment piece were empty.
Superphosphoric acid	A product of about 70 percent P_2O_5, containing polyphosphoric acids. Made by burning elemental phosphorus in the presence of water or by evaporating wet-process acid in evaporators of special design.
Transfer unit	A number expressing the difficulty in absorbing a solute from a gas. It increases with the required degree of reduction in solute concentration and with reduction in the driving force for absorption. Applied to particulates, it is the numerical value of the natural logarithm of

	the reciprocal of the fraction passing through the scrubber.
TSP	**Triple superphosphate, made by treating phosphate rock with wet-process phosphoric acid containing 40-49 percent P_2O_5.**
Venturi scrubber	**The jet venturi of this report is a device furnishing scrubbing water as a high velocity jet along the axis of a venturi's throat. This action causes gas to be drawn into the venturi, where particulates are removed by impaction and soluble gases by absorption in the water droplets.**

APPENDICES

A. EMISSION AND OPERATING DATA FOR WET-PROCESS PHOSPHORIC ACID PLANTS

B. SAMPLING AND ANALYTICAL TECHNIQUES

C. WET-PHOSPHORIC ACID ESTABLISHMENTS IN U.S.

D. PHYSICAL DATA

APPENDIX A.
EMISSION AND OPERATING DATA FOR WET-PROCESS PHOSPHORIC ACID PLANTS

The data of Tables A-1 and A-2 represent emission data and analytical results from actual stack samples representing approximately 10 percent of the current number of establishments in the United States. The stack sampling program was carried out by Public Health Service personnel. Data for plants 11 through 14 of Table A-3 are from private communications. Data for plants 15 and 16 were obtained in response to a questionnaire submitted to producing plants. Table A-4 is derived from a paper by Huffstutler and Starnes.[17]

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Table A-1. PERFORMANCE OF EMISSION CONTROL EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS-GASEOUS AND PARTICULATE FLUORIDE EMISSION DATA

Plant number	1		1		1		1			2		
Plant type	Chemico		Chemico		Chemico		Chemico			Dorr-Oliver		
Related capacity, tons/day P_2O_5	100		100		100		100			150		
Production, tons/day P_2O_5	107.5		107.5		107.5		107.5			156		
Gas scrubber type	Rectangular spray chamber		Rectangular spray chamber		Rectangular spray chamber		None			Square horizontal spray duct		
Scrubber water, gpm												
Emission source	Digester		Digester		Digester		Filter			3 digesters		
Test location	Spray chamber		Spray chamber		Spray chamber		Filter hood			Spray duct		
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Outlet			Outlet		
Gas temperature, °F		160		160		160		80			75	
Dry gas rate[a], scfm		3,675		3,843		3,877	5,970	6,604	6,507	22,870	22,840	22,070
Gaseous fluoride,												
lb/day	136	58.3	202	56.2	232	68	5.1	5.6	5.7	15.2	15.8	10.2
lb/ton P_2O_5 produced	1.265	0.54	1.87	0.52	2.16	0.63	0.047	0.053	0.053	0.097	0.101	0.072
grain/scf	0.190	0.082	0.270	0.075	0.306	0.090	0.0044	0.0044	0.0045	0.0033	0.0035	0.0026
Efficiency, %	57.1		72.2		70.7							
Particulates (total),												
lb/day		45.8		53.7		30.0	18	21.2	22.1	56.8	57.8	73.3
lb/ton P_2O_5 produced		0.430		0.500		0.280	0.170	0.200	0.210	0.360	0.370	0.470
grain/scf		0.064		0.072		0.040	0.015	0.017	0.017		0.013	0.470
Efficiency, %												
Soluble fluoride particulates,												
lb/day		10.07		9.67		5.34	0.760	0.867	0.973	5.71	5.37	1.17
lb/ton P_2O_5 produced		0.094		0.090		0.050	0.0071	0.0081	0.0091	0.036	0.034	0.0075
grain/scf		0.014		0.0133		0.0071	0.00065	0.00067	0.00077	0.0013	0.0012	0.00027
Efficiency, %												
Insoluble fluoride particulates,												
lb/day		0.643		0.068		0.841	0.094	0.027	0.378	none		0.062
lb/ton P_2O_5 produced		0.0060		0.0063		0.0078	0.00087	0.00025	0.00350		0.0013	0.00040
grain/scf		0.00090		0.000091		0.0011	0.000081	0.000021	0.0008			
Efficiency, %												

[a] 60 °F and 29.92 in. Hg.

Table A-1 (continued). PERFORMANCE OF EMISSION CONTROL EQUIPMENT IN WET-PROCESS PHOSPHORIC ACID PLANTS-GASEOUS AND PARTICULATE FLUORIDE EMISSION DATA

Plant number	3		3		3		10		
Plant type	Prayon		Prayon		Prayon		Prayon		
Rated capacity, tons/day P_2O_5	100		100		100		150		
Production, tons/day P_2O_5	130		130		130		150		
Gas scrubber type	Venturi, water-actuated		Venturi, water-actuated		Venturi, water-actuated		Spray cross-flow packed		
Scrubber water, gpm	400		400		400		420		
Emission source	Digester		Digester		Digester		Digester, filter, accessories		
Test location	Venturi		Venturi		Venturi		Scrubber		
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Outlet		
Gas temperature, °F	130	130	132	130	135	135	102	102	102
Dry gas rate,[a] scfm	1,987	1,751	2,588	2,146	1,968	1,770	8,527	8,535	8,478
Gaseous fluoride,									
lb/day	40.3		39.0	6.16	27.4	3.58	23.6	23.2	20.3
lb/ton P_2O_5 produced	0.31		0.30	0.047	0.211	0.0275	0.157	0.155	0.135
grain/scf	0.104		0.077	0.0147	0.071	0.0104	0.014	0.014	0.012
Efficiency, %			84.2		87.0				
Particulates (total),									
lb/day	593	none detected	240	3.7	1,430	0.306	54.8	44.2	44.2
lb/ton P_2O_5 produced	4.550		1.850	0.029	11	0.0024	0.364	0.294	0.294
grain/scf	1.550		0.476	0.0088	3.730	0.00089	0.0312	0.0252	0.0252
Efficiency, %	100[b]		98.5		99.97				
Soluble fluoride particulates,									
lb/day	10.1	0.30	8.0	0.37	5.12	0.307	18.5	21.4	11.0
lb/ton P_2O_5 produced	0.078	0.0023	0.062	0.0029	0.039	0.0024	0.123	0.142	0.073
grain/scf	0.026	0.00088	0.016	0.00088	0.013	0.00089	0.011	0.013	0.0067
Efficiency, %	97.0		95.4		94.0				
Insoluble fluoride particulates,									
lb/day	40.6	none detected	8.85	none detected	10.6	none detected	8.85	0.84	13.7
lb/ton P_2O_5 produced	0.310		0.068		0.082		0.059	0.0056	0.091
grain/scf	0.105		0.0175		0.028		0.0054		0.0083
Efficiency, %	100[b]		100[b]		100[b]				

[a] 60 °F and 29.92 in. Hg.

[b] Essentially complete removal.

Table A-2. GASEOUS FLUORIDE EMISSION DATA FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	4		4		4	
Plant type	Prayon one reactor		Prayon one reactor		Prayon one reactor	
Rated capacity, tons/day P_2O_5	450		450		450	
Production, tons/day P_2O_5	639		639		639	
Gas scrubber type	Venturi, water-actuated		Venturi, water-actuated		Venturi, water-actuated	
Scrubber water, gpm	475		475		475	
Emission source	Digester		Digester		Digester	
Test location	Venturi		Venturi		Venturi	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Gas temperature, °F		84		84		84
Dry gas rate, scfm	5,281	5,281	5,281	5,281	5,281	5,281
Gaseous fluoride						
lb/day	398	20.9	425	18.2	313	24.1
lb/ton P_2O_5 produced	0.62	0.033	0.67	0.028	0.49	0.038
grain/scf	0.388	0.020	0.414	0.018	0.304	0.023
Efficiency, %	94.75		95.7		92.3	

Table A-2 (continued). GASEOUS FLUORIDE EMISSION DATA FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	5				5				5			
Plant type	Prayon				Prayon				Prayon			
Rated capacity, tons/day P_2O_5	660				660				660			
Production, tons/day P_2O_5	700				700				700			
Gas scrubber type	Separate gas feeds, spray cross-flow packed				Separate gas feeds, spray cross-flow packed				Separate gas feeds, spray cross-flow packed			
Scrubber water, gpm	800				800				800			
Emission source	Digester	Filter	Combined digester and filter	Scrubber	Digester	Filter	Combined digester and filter	Scrubber	Digester	Filter	Combined digester and filter	Scrubber
Test location	Scrubber	Scrubber		Scrubber	Scrubber	Scrubber		Scrubber	Scrubber	Scrubber		Scrubber
	Inlet	Inlet	Inlet	Outlet	Inlet	Inlet	Inlet	Outlet	Inlet	Inlet	Inlet	Outlet
Gas temperature, °F	145			90	145			90	145			90
Dry gas rate, scfm	7,500	12,231	19,731		7,500	12,231	19,731		7,500	12,231	19,731	
Gaseous fluoride lb/day	41.5	19.4	60.9	12.3	38.8	16.0	54.8	5.9	46.6	8.0	54.6	4.15
lb/ton P_2O_5 produced	0.059	0.028	0.087	0.018	0.056	0.023	0.078	0.0085	0.067	0.011	0.078	0.0060
grain/scf	0.028	0.0081	0.016	0.0032	0.027	0.0067	0.014	0.0015	0.032	0.0038	0.014	0.0011
Efficiency, %	79.6				89.3				92.4			

Table A-2 (continued). GASEOUS FLUORIDE EMISSION DATA FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	6				6				6			
Plant type	Dorr-Oliver				Dorr-Oliver				Dorr-Oliver			
Rated capacity, tons/day P_2O_5	1,200 two lines @ 600				1,200				1,200			
Production, tons/day P_2O_5	1,080				1,080				1,080			
Gas scrubber type	Doyle (two in series)				Doyle (two in series)				Doyle (two in series)			
Emission source	Acid line No. 1	Acid line No. 2	Combined lines 1 and 2	Scrubber	Acid line No. 1	Acid line No. 2	Combined lines 1 and 2	Scrubber	Acid line No. 1	Acid line No. 2	Combined lines 1 and 2	Scrubber
Test location	Scrubber	Scrubber		Scrubber	Scrubber	Scrubber		Scrubber	Scrubber	Scrubber		Scrubber
	Inlet	Inlet	Inlet	Outlet	Inlet	Inlet	Inlet	Outlet	Inlet	Inlet	Inlet	Outlet
Gas temperature, °F	82	100			82	100			82	100		
Dry gas rate, scfm	8,300	8,370	16,670	16,670	8,300	8,370	16,670	16,670	8,300	8,370	16,670	16,670
Gaseous fluoride												
lb/day	3.6	10.8	14.4	12.2	5.4	11.6	17.0	6.5	3.5	11.6	15.1	7.8
lb/ton P_2O_5 produced			0.0133	0.0112			0.0158	0.0060			0.0140	0.0072
grain/scf	0.0022	0.0066	0.0044	0.0037	0.0033	0.0071	0.0052	0.0020	0.0022	0.0071	0.0047	0.0024
Efficiency, %	15				62				48			

Table A-2 (continued). GASEOUS FLUORIDE EMISSION DATA FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	7				7				7			
Plant type	Prayon				Prayon				Prayon			
Rated capacity, tons/day P_2O_5	400				400				400			
Production, tons/day P_2O_5	400				400				400			
Gas scrubber type	Separate gas feeds, spray cross-flow packed				Separate gas feeds, spray cross-flow packed				Separate gas feeds, spray cross-flow packed			
Scrubber water, gpm	800				800				800			
Emission source	Sump and vent	Digester	Filter		Sump and vent	Digester	Filter		Sump and vent	Digester	Filter	
Test location	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber
	Inlet	Inlet	Inlet	Outlet	Inlet	Inlet	Inlet	Outlet	Inlet	Inlet	Inlet	Outlet
Gas temperature, °F	70	140		85	70	140		85	70	140		85
Dry gas rate, scfm[a]	14,100	16,200	9,700	40,000[b]	14,100	16,200	9,700	40,000[b]	14,100	16,200	9,700	40,000[b]
Gaseous fluoride												
lb/day	10.6	460	10.9	68	9.7	571	12.1	63	16.9	548	9.6	42
lb/ton P_2O_5 produced	0.026	1.15	0.027	0.170	0.024	1.43	0.030	0.157	0.042	1.37	0.024	0.105
grain/scf	0.0038	0.145	0.0058	0.0088	0.0035	0.180	0.0064	0.0081	0.0062	0.173	0.0051	0.0054
Efficiency, %	85.9				89.4				92.7			

[a] 60 °F and 29.92 in. Hg.

[b] Contains approximately 13 ppm SO_2.

Table A-2 (continued). GASEOUS FLUORIDE EMISSION DATA FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	8				8				8			
Plant type	Prayon				Prayon				Prayon			
Rated capacity, tons/day P_2O_5	750				750				750			
Production, tons/day P_2O_5	745				745				745			
Gas scrubber type	Separate gas feeds, spray cross-flow packed				Separate gas feeds, spray cross-flow packed				Separate gas feeds, spray cross-flow packed			
Scrubber water, gpm	960 - 1,200				960 - 1,200				960 - 1,200			
Emission source	Filter	Digester	Combined digester and filter	Scrubber	Filter	Digester	Combined digester and filter	Scrubber	Filter	Digester	Combined digester and filter	Scrubber
Test location	Scrubber	Scrubber		Scrubber	Scrubber	Scrubber		Scrubber	Scrubber	Scrubber		Scrubber
	Inlet	Inlet	Inlet	Outlet[c]	Inlet	Inlet	Inlet	Outlet[c]	Inlet	Inlet	Inlet	Outlet[c]
Gas temperature, °F	95	150		95	95	150		95	95	150		95
Dry gas rate, scfm[a]	19,600	10,000		29,600	19,600	10,000		29,600	19,600	10,000		29,600
Gaseous fluoride												
lb/day	8.2	30.2	38.4	16.6	14.1	27.6	41.7	13.2	8.3	28.4	36.7	12.7
lb/ton P_2O_5 produced	0.011	0.040	0.051	0.022	0.019	0.037	0.056	0.0177	0.011	0.038	0.049	0.0170
grain/scf	0.0021	0.0154	0.0067	0.0029	0.0037	0.014	0.0072	0.0023	0.0022	0.0145	0.0063	0.0022
Efficiency, %	56.7				68.4				65.4			

[a] 60 °F and 29.92 in. Hg.

[c] Contains 6-18 ppm SO_2.

Table A-2 (continued). GASEOUS FLUORIDE EMISSION DATA FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	9				9				9			
Plant type	Prayon				Prayon				Prayon			
Rated capacity, tons/day, P_2O_5	76.5				76.5				76.5			
Production, tons/day, P_2O_5	103				103				103			
Gas scrubber type	Cyclonic spray tower				Cyclonic spray tower				Cyclonic spray tower			
Scrubber water, gpm	900				900				900			
Emission source	Sump and vent	Digester	Filter	Tower	Sump and vent	Digester	Filter	Tower	Sump and vent	Digester	Filter	Tower
Test location	Tower				Tower				Tower			
	Inlet	Inlet	Inlet	Outlet[a]	Inlet	Inlet	Inlet	Outlet[a]	Inlet	Inlet	Inlet	Outlet[a]
Gas temperature, °F	88		90	90	88		90	90	88		90	90
Dry gas rate, scfm	5,730	6,130	3,440	15,300	5,730	6,130	3,440	15,300	5,730	6,130	3,440	15,300
Gaseous fluoride												
lb/day	25.4	59	3.5	8.4	25.0	74	4.3	6.8	26.6	70.3	6.5	4.8
lb/ton P_2O_5 produced	0.247	0.573	0.034	0.082	0.243	0.718	0.042	0.066	0.258	0.683	0.063	0.047
grain/scf	0.023	0.049	0.0052	0.0029	0.022	0.062	0.0064	0.0023	0.024	0.059	0.0094	0.0016
Efficiency, %	90.4				93.4				95.3			

[a] Contains 1-2 ppm SO_2.

Table A-3. GASEOUS AND TOTAL FLUORIDE EMISSIONS FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	11[a]		12[a]		13[a]	
Plant type						
Rated capacity, tons/day P_2O_5						
Production, tons/day P_2O_5	460		550		450[c]	
Gas scrubber type	Water-actuated venturi		Cyclonic spray		Spray cross-flow packed	
Scrubber water, gpm	1,040		470-550		690	
Scrubber ΔP, inches H_2O	1		3-5		6-10	
Emission source	Digester and filter		Digester and filter		Digester and filter	
Test location	Scrubber		Scrubber		Scrubber	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Gas temperature, °F						
Wet-gas flow rate, scfm	10,000		108,000		30,000	
Total fluoride, lb/day						
lb/ton P_2O_5						
grain/scf						
ppm						
Gaseous and water-soluble particulate fluoride, lb/day	900	120	4,200	680	240	20
lb/ton P_2O_5	2.0	0.26	7.6	1.23	0.53	0.044
grain/scf	0.45	0.058	0.19	0.031	0.039	0.0032
ppm	1,280	167	540	87	108	9
Efficiency, %	87		84		92	

[a] Data received in private communication.

[b] Data received by questionnaire.

[c] Two separate plants, using different processes.

Table A-3 (continued). GASEOUS AND TOTAL FLUORIDE EMISSIONS FROM WET-PROCESS PHOSPHORIC ACID PLANTS

Plant number	14[a]		15[b]		16[b]
Plant type			Dorr-Oliver multi-tank		Dorr-Oliver single tank
Rated capacity, tons/day P_2O_5			900		650
Production, tons/day P_2O_5	450[c]		1,035		650
Gas scrubber type	Spray cross-flow packed		Impingement	None	Train 1 - packed tower Train 2 - two-stage cyclonic scrubber
Scrubber water, gpm	800				
Scrubber ΔP, inches H_2O	6-10				
Emission source	Digester and filter		Digester and filter		Digester
Test location	Scrubber		Scrubber		Combined scrubber
	Inlet	Outlet	Outlet	Outlet	Outlet
Gas temperature, °F			96	95	96
Wet-gas flow rate, scfm	43,000		21,170	29,000	66,000
Total fluoride,					
lb/day			38	80	5
lb/ton P_2O_5			0.037	0.077	0.0073
grain/scf			0.0087	0.01	0.00035
ppm			24	38	1
Gaseous and water-soluble particulate fluoride,					
lb/day	34,600	17			
lb/ton P_2O_5	77	0.038			
grain/scf	3.9	0.0019			
ppm	10,000	5			
Efficiency, %	99.9				

[a] Data received in private communication.

[b] Data received by questionnaire.

[c] Two separate plants, using different processes.

Table A-4. WET-PROCESS PHOSPHORIC ACID PLANT FLUORIDE EMISSIONS AFTER CONTROL UNITS[17]

Plant production capacity, P_2O_5 tons/day	Fluoride emissions[a]					
	Company reported			Florida State Board of Health reported		
	lb/hr	lb/day	lb/ton P_2O_5	lb/hr	lb/day	lb/ton P_2O_5
Reactors and filters[b]						
500	0.407	9.8	0.020	1.750	42.0	0.084
400	1.000	24.0	0.060	2.660	64.0	0.135
300	0.685	16.5	0.055	0.040	0.96	0.0032
170	0.145	3.5	0.020	1.090	26.0	0.153
Reactors only[b]						
260	0.740	17.8	0.055	0.055	1.33	0.0051
200	0.750	18.0	0.090	0.234	5.6	0.028
175	0.133	3.2	0.018	1.700	40.8	0.23

[a] Gaseous fluorides and water-soluble particulate fluoride only.

[b] Controlled sources.

APPENDIX B.
SAMPLING AND ANALYTICAL TECHNIQUES

INTRODUCTION

The sampling equipment for this study was constructed by the Public Health Service for the specific task of measuring air pollutant emissions at their sources. The following description of the apparatus is general. The reader is referred to APCA Journal, 18(1):12-14 for a more complete discussion of stack-gas testing. The basic measurements performed during this sampling were of effluent flow, and gaseous and particulate fluoride concentrations.

The overall, source-testing procedure may be divided into three major phases: preliminary survey, field sampling, and laboratory analysis.

Preliminary surveys were done well in advance of the actual tests. The purpose was to determine which type of pollutant to measure and to arrange the logistics involved in conducting a source test. The source test itself was composed of several components, including set-up for operation, and sample clean-up. Since the sampling trains differ, gaseous and particulate sampling will be discussed separately.

THEORY OF SAMPLING TRAIN DESIGN

There are two types of sampling trains - gaseous and particulate - and each contains a heated and a cooled section. The glass probes and filtering elements of both trains are electrically heated to 250° F. Both trains have gas impingement systems that are cooled by ice bath. These two systems are similar for distinct chemical reasons.

The glass probe is heated to 250° F to cause reaction to occur between the hydrogen fluoride in the sample-gas stream and the silicon dioxide in the glass walls of the probe. The reaction is:

$$4HF + SiO_2 \xrightarrow{250°\ F} SiF_4\,(g) + 2H_2O(g)$$

Because further reaction occurs in cool water, the filtering element is also heated to 250° F in order to prevent water condensing on the filter and clogging the pores of the paper. The heated probe and filter arrangement also prevent the hydrogen fluoride gas from reacting with the filter or filtered media.

Both trains use gas impingers with a collecting medium of chilled water. Water is used as the absorbing agent because fluorides are highly soluble in water. The gases pass into this ice-bath-cooled section and the silicon tetrafluoride gas hydrolyzes in the water to the final stable products, soluble fluosilicic acid and slightly soluble orthosilicic acid. The reaction is:

$$3\ SiF_4 + 4H_2O \longrightarrow 2H_2\ SiF_6 + \underset{\displaystyle H_2O + SiO_2}{\underset{\big\downarrow}{Si\ (OH)_4}}$$

The formation of silicon dioxide, a gelantinous precipitate, makes it necessary to remove the nozzle tip from the first impinger. If this were not done, the nozzle tip could become clogged after a few minutes of sampling.

PARTICULATE-MATTER SAMPLING PROCEDURE

The sampling tests are performed isokinetically along a representative traverse of the stack. The equipment, shown in Figures B-1, B-2, and B-3, is assembled as shown with the heated box, ice bath, and glassware designed to move with the probe. The probe is kept

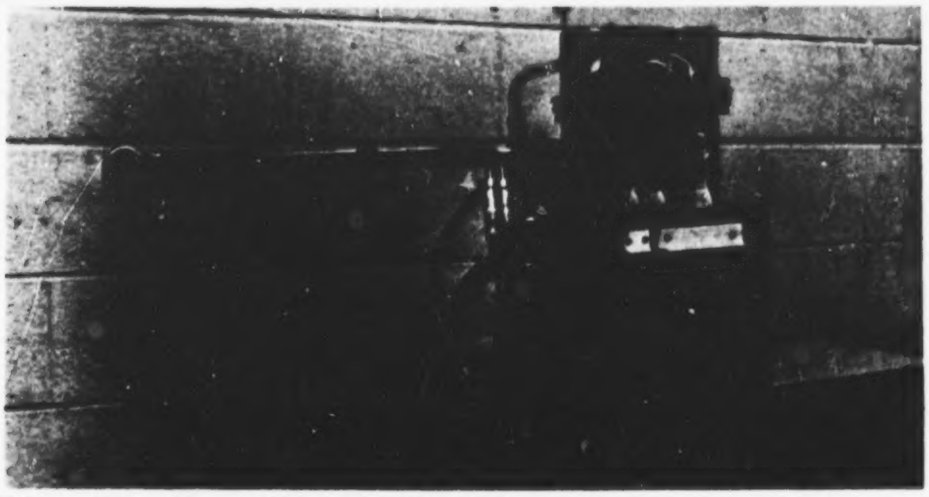

Figure B-1. Sample box with pitot tube, impingers, and umbilical cord.

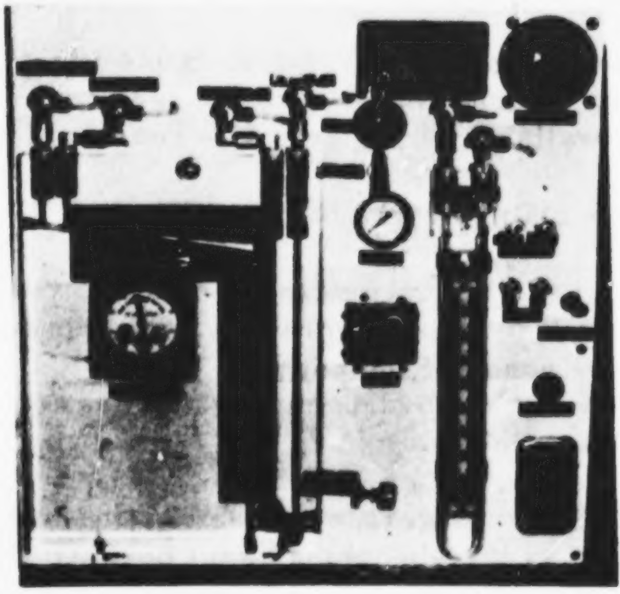

Figure B-2. Meter box controls.

sufficiently hot to avoid condensation and to cause the fluoride-silica reaction to occur. The remainder of the equipment is placed at some convenient location and connected by the rubber umbilical hose. A probe tip is selected so that isokinetic sampling will be maintained at approximately 0.75 cubic foot per minute. This flow rate approximates the design flow rate through cyclone and Greenburg-Smith impingers. Thus, a flow rate of 0.75 cubic foot per minute provides an efficient separation of gaseous and particulate pollutants.

Adjustment to isokinetic conditions is accomplished by use of a needle valve and a bypass gate valve. At any instant, the dry-gas sampling rate may be determined from the inclined-vertical manometer, which is connected across a calibrated orifice. A conversion from the dry-gas sampling rate to the total-gas sampling rate is made, by correcting for moisture condensed and absorbed from the stack effluent by the impingers and silica gel; or generally from the preliminary wet- and dry-bulb measurements. In the case of wet-process phosphoric acid manufacture, fluorine compounds found in the stack gas are not a significant part of the gas volume sampled and need not be considered in calculating total volume.

The thermometer in the cap of the outlet of the fourth impinger indicates the ice-bath efficiency. This temperature is important, in that if it goes above 70° F the ice bath is no longer serving its function and all of the moisture may not be removed. The volume of gas sampled at each point of the traverse is determined by reference to the indicated values on the dry-gas meter, to assure that the calibrated orifice is operating properly. The temperature of the dry gas in the meter is obtained by averaging the meter inlet and outlet thermometer temperatures. This temperature is necessary to calculate the gas-sample volume at standard conditions of temperature and pressure.

Particulate-Matter Sampling Apparatus

The particulate-matter sampling apparatus (shown in Figure B-3) consists of a probe, a cyclone, a filter, four Greenburg-Smith impingers, a flowmeter, a manometer, a dry-gas meter, and an air pump. The stainless steel, button-hook-type probe tip (1)* is drawn to 5/8 inch so that it will connect, by a stainless steel coupling (2) with a Viton "O" ring bushing, to the probe (3). The probe (3) is fabricated of 5/8 inch, medium-wall, Pyrex glass tube with a 28/12 ball joint on one end. The glass probe is wound with 25 feet of 26-guage Nichrome wire. The Nichrome-wound glass tube is wrapped with a fiber-glass tape, and during the sampling the Nichrome wire is connected to a variable auto-transformer so that the amount of heat transmitted to the probe can be controlled. The wire-wound probe is encased in a 1-inch stainless steel tube. The front end of the tube has a nut welded to it for connection to the stainless steel coupling and nozzle tip. The probe connects to a cyclone and flask (4). The cyclone is described in detail in Reference 5, except for the 28/12 female ball joint on the arm. The

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*Numbers in parentheses refer to numbered parts of Figure B-3.

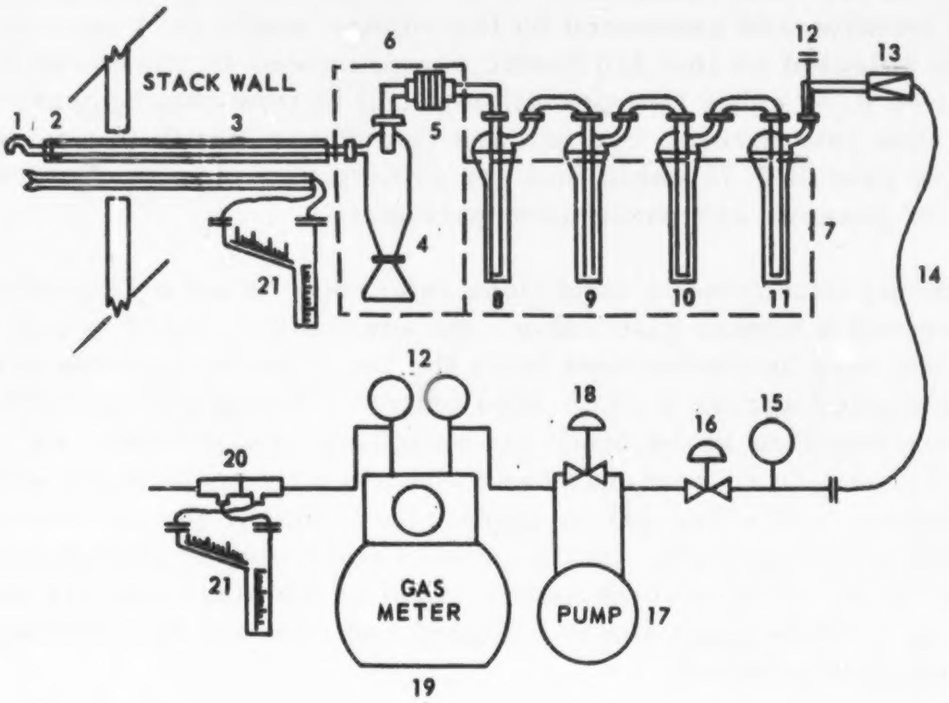

Figure B-3. Particulate sampling train.

cyclone is designed to provide a particulate separation with a size cut of 5 microns. It is connected to a fritted glass filter (5) which holds a 2-1/2 inch, Number 41 Whatman filter paper. The cyclone, flask, and filter are contained in an electrically heated enclosed box. The flow of sample gas leaves the heated-particulate-filtering system and passes into the ice-bath-cooled, gas-impingment section. The first impinger (8) of this system is of the Greenburg-Smith design, modified by replacing the orifice plate tip with a 1/2-inch I D glass tube extending to one-half inch from the flask bottom.

This impinger is filled with 250 milliliters of deionized water. The second impinger (9) is a standard Greenburg-Smith impinger filled with 150 milliliters of deionized water. The third impinger (10) is a Greenburg-Smith impinger modified like the first. This impinger is left dry to collect any entrainment. The fourth impinger (11) is also a Greenburg-Smith impinger modified like the first. This impinger contains approximately 175 grams of accurately-weighed dry silica gel. From the fourth impinger (11), the effluent stream flows through a check valve (13) to a flexible rubber vacuum tubing (14). The sample gas goes through a needle valve (16) and then a vacuum pump (17), rated at 4 cubic feet per minute at 0 inches of mercury gauge pressure, which is in parallel with a bypass gate valve (18); a dry-gas test meter (19), with a scale of 1 cubic foot per revolution is used to record the volume sampled. The three thermometers (12) are dial type with a range from 25° to 125° F and having a 5-inch stem. The vacuum gauge (15) is calibrated from 0 through 30 inches of mercury. The manometers (21) across the calibrated orifice (20) and pitotmeter (22) are the inclined-vertical type, graduated in hundreths of an inch of water from 0 to 1.0 inch, and in tenths from 1 to 10 inches.

DISCUSSION OF GAS SAMPLING

The gas sampling train, since it does not sample isokinetically is much simpler in operation and theory. There is no concentration gradient of gaseous fluorides in a well-mixed stack gas, so the probe may be held stationary. The fact that no traversing is required allows the probe impingers and ice bath to be securely fastened to the wall of the stack. This is done with an ell-shaped platform which is designed to be strapped to the flue. The sample-gas rate is metered at another, more convenient location. This gas flow is carried in a vacuum-hose umbilical cord which also carries the wires that supply electricity to heat the probe and filtering elements. The midget impingers that are used were designed to absorb gases most efficiently at a sampling rate of 0.1 cubic foot per minute. The sample flow rate is accordingly maintained near this value by checking a small air rotameter, and making adjustments as needed. Emission rates are generally expressed on a dry basis. This is done to prevent changes in scrubber-gas moisture content from altering the control efficiency of the unit. The stack moisture is determined from wet- and dry-bulb temperature measurements which are made during the preliminary test. This is also the time at which the velocity traverse of the stack is made. The traverse is done with the most accurate methods available using the technique described in Los Angeles Source Testing Manual.

In the actual procedure for gas sampling, the amount of sample gas withdrawn from the flue is not critical. The major considerations are that an accurately measured amount of fluoride be absorbed in the impinger water and that there be enough time to provide an average response in the process. Hence, the samples are generally taken over a 15-minute period.

Apparatus for Gas Sampling

The apparatus for gaseous fluoride sampling (Figures B-4, B-5) is considerably simpler and more portable than the particulate train. The gas train is composed of a probe (1)*, filter (4), impingers (6, 7, 8, 9), pump (13), rotometer (15), and dry-gas test meter (17). More specifically, the sample is first drawn in through a two-foot medium-wall Pyrex glass probe (1) which is wound with 18 feet of 26-guage Nichrome heating wire (2). This wire is connected to a variable transformer (3) which allows the voltage and hence the heat input to be controlled. The wire is covered with a fiber glass insulation tape and placed in a stainless steel probe sheath.

A Gelman #4300 pressure filtration funnel (4) is next in line. It is wire-wrapped, as the probe is, and contains a 1-inch, Whatman #41 filter paper. It is in this manner that the sample gas is heated so

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*Number in parentheses refer to numbered parts of Figure B-5.

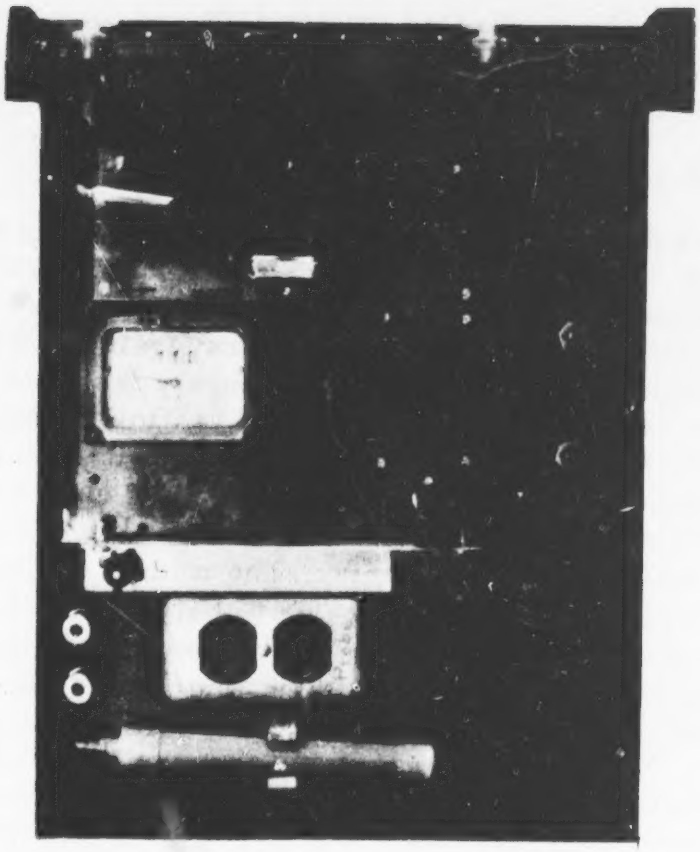

Figure B-4. Gas sampling train.

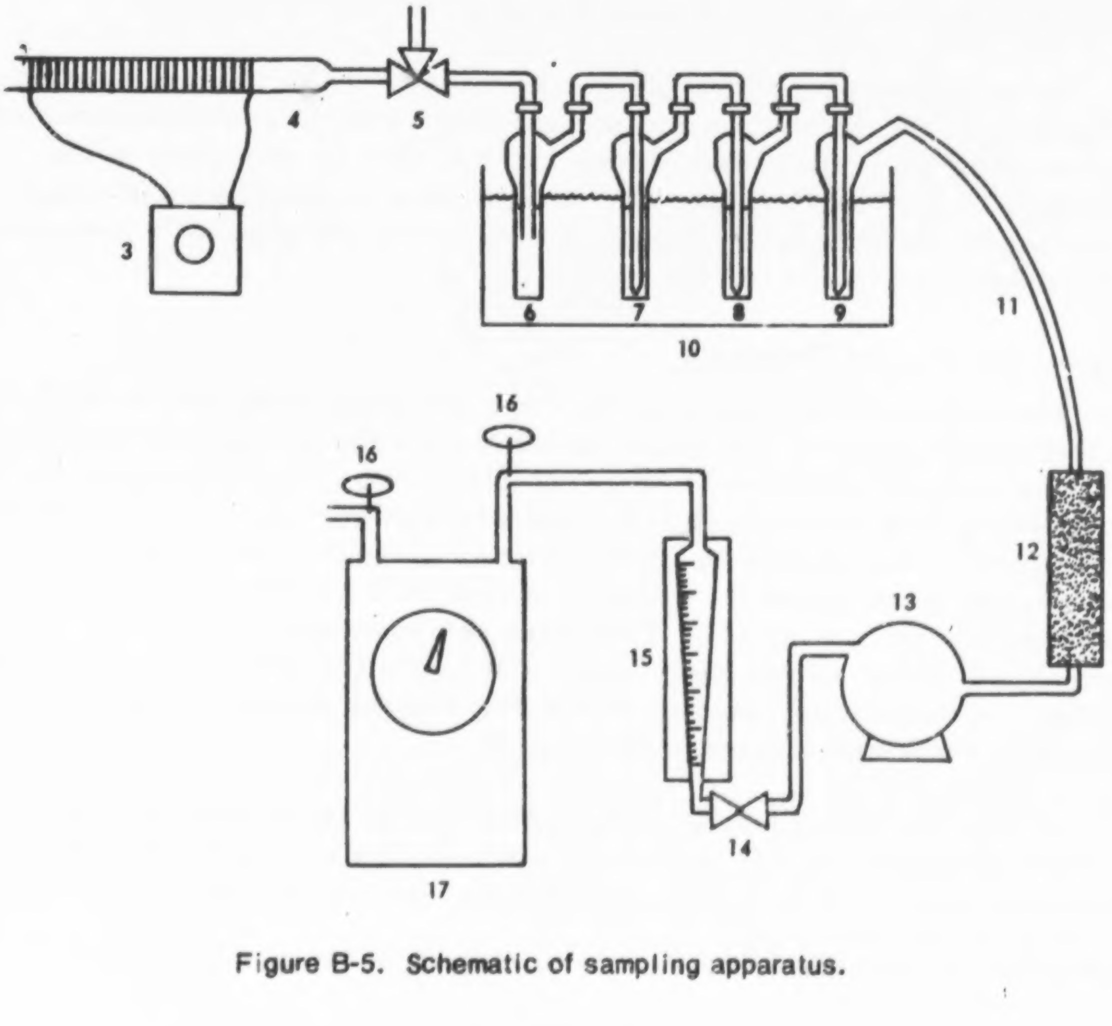
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Figure B-5. Schematic of sampling apparatus.

that moisture will not clog the filter and the gaseous fluorides will react with the glass of the probe to form a water-soluble compound (silicon tetrafluoride). A three-way valve (5) is used to purge the line before the actual sampling begins. This valve also allows the ice bath (10) and impinger system to be sealed off and removed after the run is completed. The heated sample gas now enters the impinger system where the soluble fluorides are scrubbed out. Due to the sensitivity of the analytical method only a small sample is required, therefore, four midget impingers are used. The first three impingers (6, 7, 8) contain approximately 15 milliliters of distilled water with the nozzle tip of the first impinger removed to prevent silicon dioxide (a byproduct of the glass-fluoride reaction) from clogging the opening. The fourth impinger (9) is left dry and is used to collect any entrained water. The scrubbed gas flows from the collecting media through an umbilical cord to a silica-gel-packed drying tube (12) which removes the moisture from the sample gas. A diaphragm pump (13) is used to pull the gas through this system. From the pump the gases pass through a gross-flow control rotometer (15) with the needle valve (14) of the rotometer normally set to maintain a sampling rate at 0.1 cubic foot per minute. The actual sample volume is read from a dry-gas meter (17) with an accuracy of plus and minus 1 percent. The dry-gas meter is fitted with thermometers (16) on the meter inlet and outlet sides. These thermometers give the gas temperature inside the meter, allowing correction of the sample volume to standard conditions.

CONSIDERATIONS COMMON TO GASEOUS AND PARTICULATE SAMPLING

Selection of Sampling Points

The locations and number of sampling points are based on size and shape of the duct, uniformity of gas flow, availability of sampling port, and space required to set up sampling equipment. Straight vertical ducts with no flow obstructions for at least eight diameters upstream and two diameters downstream of the sampling point are preferred.

To insure a representative sample of stack gas, the duct should be divided into a number of equal areas and sampled at the center of each of these areas. The number of areas depends on the size of the stack. It is also desirable to sample across the largest dimension of the stack. Horizontal flues should be sampled in the vertical direction to prevent erroneous results due to stratification of the particulates in the duct. The number of areas into which the duct area was divided for the sampling was decided on the basic of criteria discussed in Western Precipitation Company's Bulletin WP-50.

Sampling Time and Equipment Cost

The time necessary to perform the series of triplicate tests at each point is determined largely by engineering ingenuity. However, through the use of packaged sampling equipment, designed on the basis of a thorough preliminary survey, the time required for the field assembly of sampling equipment can be greatly reduced. Thus, it should rarely take over two man-days for a sample point to be tested from start to finish.

The cost of specific particulate-matter sampling equipment, enough material and apparatus for three replicate tests, would be approximately \$3,000. But, for approximately another \$1,000, additional equipment could be purchased so that virtually all types of particulate matter and acid mists could be collected.

The gas sampling train is considerably less expensive. Necessary train components and glassware for three runs should not cost more than \$400.

Field Calculations

The mathematical development of the field calculations necessary for the proper operation of this isokinetic, particulate sampler will be discussed in this section. The gaseous train requires no field calculations as no adjustments have to be made once the flow is adjusted to 0.1 cubic foot per minute. The particulate train, on the other hand, must be able to sample at various volumetric rates depending on changes in the stack-gas velocity. The following material explains how and why these rate changes are made.

Isokinetic sampling requires that the sampling velocity through the nozzle be equal to the effluent velocity in the stack. The nozzle velocity is determined from the volumetric sampling rate. Both stack velocity (measured by the pitometer) and volumetric sampling rate (measured by the calibrated-orifice) are indicated by manometer pressure differences. For isokinetic sampling, the calibrated-orifice manometer is made dependent on the pitometer-manometer by combining the pitometer equation;

$$V_p = C_p \sqrt{\frac{2g_c \, \Delta P R T_s}{P_s \, M_s}} \qquad (1)$$

with an equation relating volumetric sampling rate to effluent velocity through the nozzle:

$$Q_m = \frac{\pi}{4} D^2 \, V_p \frac{T_m}{T_s} \, \frac{P_s}{P_m} M_c \qquad (2)$$

where: C_p = pitometer calibration factor, dimensionless
g_c = gravitational constant, 32.17 $(\mathrm{lb_{mass}})\ (\mathrm{ft})/(\mathrm{lb_{force}})\ (\mathrm{sec}^2)$
ΔP = pitometer pressure differential, $(\mathrm{lb_{force}})/(\mathrm{ft}^2)$
R = gas-law constant, 1545 (ft) $(\mathrm{lb_{force}})/(°\mathrm{R})$ (lb-mole)
T_s = stack gas temperature, °R
P_s = stack gas pressure, $(\mathrm{lb_{force}})/(\mathrm{ft}^2)$
M_s = effluent molecular weight, $(\mathrm{lb_{mass}})/(\mathrm{lb\text{-}mole})$
Q_m = volumetric flow rate, $\mathrm{ft}^3/\mathrm{sec}$
D = nozzle diameter, ft
V_p = stack velocity at traverse point, ft/sec
T_m = effluent temperature at the meter, °R

P_m = meter pressure, $(lb_{force})/(ft^2)$
M_c = mole fraction of dry gas in stack effluent, dimensionless

When a calibrated orifice is used to measure Q_m,

$$Q_m = JA\sqrt{\frac{T_m \Delta H\, 2g_c\, R}{P_m\, M_m}} \tag{3}$$

where: J = orifice coefficient, dimensionless
A = orifice area, ft^2
ΔH = orifice pressure differential, $(lb_{force})/(ft^2)$
M_m = dry effluent molecular weight, $(lb_{mass})/(lb\text{-}mole)$.

Combining and rearranging Equations, 1, 2, and 3 give the dependency of the calibrated-orifice manometer on the pitometer-manometer,

$$\Delta H = K\ (\Delta P)\, D^4\, T_s^{\ -1} \tag{4}$$

$$\text{where: } K = \left(\frac{\pi C_p M_c}{4JA}\right)^2 \frac{M_m}{M_s}\ \frac{P_s}{P_m}\ T_m \tag{5}$$

Stack-gas velocities not only change between different traverse points, but also vary at a given point because of variable flow conditions. The calculation of Equation 4 presents an undesirable time lag between changes in stack velocity and sampling rate. In addition, frequent errors are made when calculations are attempted under the stress of field sampling conditions. The net result is deviation from isokinetic sampling.

A three-independent-variable nomograph (Figure B-6) was constructed to represent Equation 5 and reduces calculation time to a few seconds. The K term in Equation 4 is usually a constant during sampling, but may change for different sampling locations or processes. A four-independent-variable nomograph could be used; but, because this would make the nomograph that much larger and unwieldy and because K does not frequently vary, K is incorporated into the T scale. This is done by making the T scale movable and setting its position with a C scale. The C scale is a ratio of the true value of K to an assumed value. If the values for K vary from the assumed values, then a new value for C is obtained from a second nomograph (Figure B-7). The nomograph of Figure B-6 is based on the assumption that the stack gas is 5 percent water, but that no water passes through the orifice. It assumes a dry-gas molecular weight of 29, atmospheric and stack pressures of 29.92 inches of mercury, a meter temperature of 70° and a $\Delta H_{@}$ (the orifice pressure differential that gives 0.75 cubic foot per minute for dry air at 70° F and 29.92 in. Hg) of 1·84. The nomograph of Figure B-7 corrects for different stack and atmospheric pressures, different stack-gas moisture contents, and different gas temperatures at the orifice. Figure B-7 does not correct for moisture in the gas passing through the orifice nor molecular weight

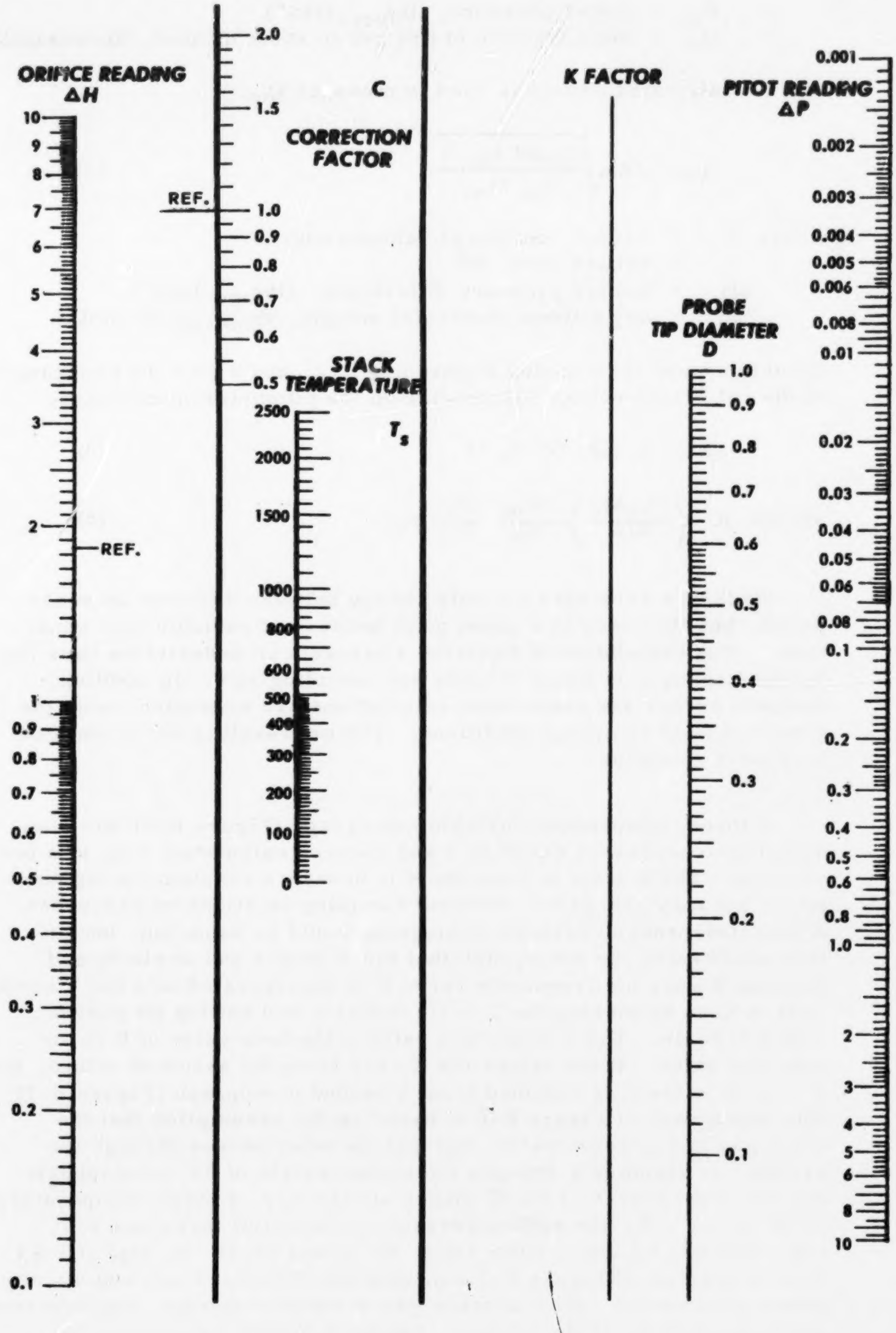
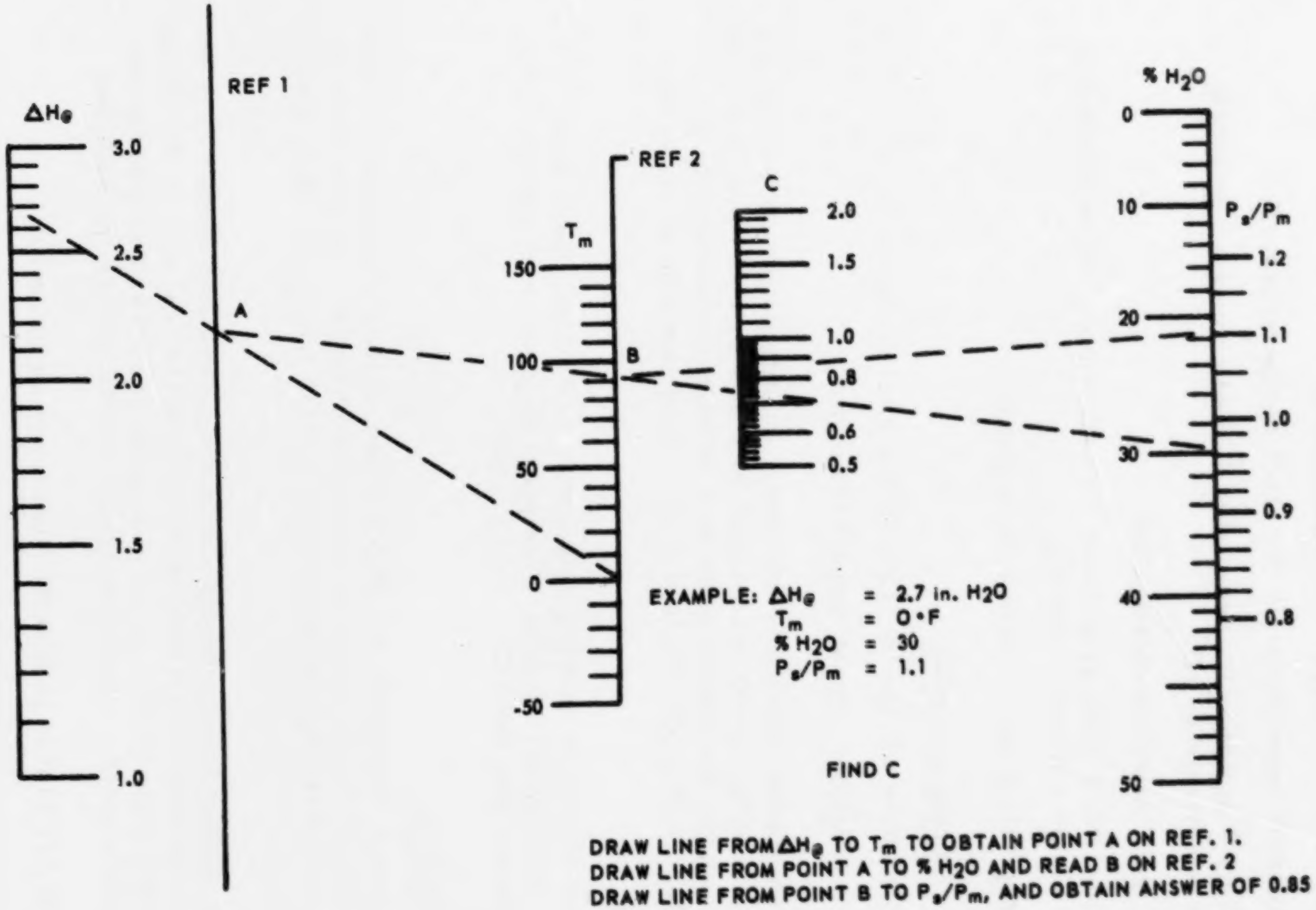


Figure B-6. Operating nomograph.



EXAMPLE: $\Delta H_@$ = 2.7 in. H_2O
T_m = 0°F
% H_2O = 30
P_s/P_m = 1.1

FIND C

DRAW LINE FROM $\Delta H_@$ TO T_m TO OBTAIN POINT A ON REF. 1.
DRAW LINE FROM POINT A TO % H_2O AND READ B ON REF. 2
DRAW LINE FROM POINT B TO P_s/P_m, AND OBTAIN ANSWER OF 0.85 FOR C.

Figure B-7. Correction factor C for figure B-6.

changes other than those due to water in the stack gas.

Directions for the use of the nomograph (Figure B-7) are as follows:

Prior to sampling

1. Obtain C from Figure B-7, and set the T scale.
2. Make a rough preliminary pitot traverse, and determine the minimum, average, and maximum ΔP.
3. Measure approximately the stack temperature, T.
4. Align T and the ΔP's from step 1, and choose a convenient nozzle diameter, D.
5. Align T and D to obtain a ΔP.
6. Align the P from step 5 and the reference point on the H line to obtain a K factor setting.
7. Keep this K factor setting as a pivot.

During sampling

8. Determine ΔH for the ΔP's of the pitot traverse.
9. If T changes, repeat steps 3 through 8.*

The nomograph calculates isokinetic conditions for an average ΔH of 1.84. This ΔH_a should correspond to a flow rate of about 0.75 cubic foot per minute if the orifice plate is 0.18 inch in diameter in a 0.5-inch I.D. tube with pressure taps 1 inch on either side of the orifice plates.

For the details of constructing nomographs the reader should consult other references, such as "Chemical Engineers Handbook," New York: McGraw-Hill Book Co., Inc., 1950.

Sampling Cleanup

This section discusses the step by step method employed to transfer the sample from the trains to storage containers. It is written in two parts, one covering the particulate-matter train, the other the gaseous train.

Particulate-matter train cleanup - It is necessary that proper care be exercised in moving the collection train from the test site to the cleanup area so that none of the collected sample is lost and so that no outside particulate matter enters the train, contaminating the samples.

Samples are placed in plastic containers as follows:

---

*It is not necessary to change the probe tip diameter, merely adjust the new temperature through the original probe tip diameter to obtain ΔP.

Container No. 1 - carefully remove the filter from the filter holder, place in the container, and seal with tape.

Container No. 2 - contains any loose particulate and acetone washings from the probe, cyclone, and cyclone flash. The inside of the cyclone and cyclone flash are brushed with a Nylon brush and the inside of the probe is brushed with a Nylon brush fitted on a stainless steel rod, to loosen adhering particles.

Container No. 3 - contains any loose particulate and acetone washings of the front half of the filter holder. The inside of this part is brushed with a Nylon brush.

Container No. 4 - the H_2O from the first three Greenburg-Smith impingers is measured to within ± 5 ml and placed in the container. H_2O rinsings from the back half of the filter holder, the fritted glass support, all connectors, and the first three Greenburg-Smith impingers are also to be placed in this container and the container sealed with tape.

Container No. 5 - the spent silica gel is weighed to the nearest 0.1 gram and then returned to a container and sealed with tape.

Gaseous train cleanup - The cleanup of the gaseous train is a simple one-step operation because only the impingers and connectors are washed out. The contents of the impingers are poured carefully into the container. The impingers and connectors are then rinsed out three times using approximately 20 milliliters of distilled water for each wash. This wash is combined with the impinger solution. The container is sealed and the top wrapped with tape.

Analysis of Particulate Matter

The following section discusses the procedure used by the laboratory in particulate fluoride analysis.

Container No. 1 - transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish and condition for 24 hours in a desiccator or constant humidity chamber containing a saturated solution of calcium chloride or its equivalent. Dry to a constant weight and record the results to the nearest 0.1 milligram.

Container No. 2 - transfer the acetone washings from the probe, cyclone, and cyclone flask, to a tared beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and dry to a constant weight. Record the results to the nearest 0.1 milligram.

Container No. 3 - transfer the acetone washings of the front half of the filter holder to a tared beaker and evaporate to dryness at ambient temperature and pressure.

Desiccate for 24 hours and dry to a constant weight. Record the results to the nearest 0.1 milligram.

Transfer all particulate samples (1, 2, 3) to a 250-ml graduated glass-stoppered cylinder, and dilute to 250 milliliters with distilled water. Shred the filter with forceps before transfer. Mix well, and transfer the total contents of the graduated cylinder to a 300-milliliter Erlenmeyer flask.

To estimate the appropriate aliquot size to be used in the distillation procedure, take a 25-milliliter aliquot of each type of sample (impinger, water-soluble particulate, total particulate) and apply the spectrophotometric procedure found in the following section on chemical fluoride analysis. From the amount of fluoride found in the undistilled aliquot, calculate the sample aliquot needed to yield 0.5 milligram of fluoride in the distilled sample.

Distillation is used to remove any interfering substances. Any chloride interferences are removed by addition of Ag_2SO_4 to the distillation mixture.

Spadns Determination of Fluorides

Introduction — This method for determining fluoride concentration is used for both particulate and gaseous fluorides. It also includes the distillation necessary to separate the fluorides from the particulate-matter samples collected. There are other methods available, but it was the one employed by the Public Health Service laboratory in analyzing the samples collected in this study.

Reagents — All chemicals used must be ACS analytical reagent grade.

Spadns solution — Dissolve 0.959 gram of 4, 5-dihydroxy-3(p-sulfophenylazo)-2, 7-napthalene disulfonic acid, and trisodium salt (Spadns), at room temperature, if protected from sunlight.[24]

Zirconyl chloride octahydrate solution — Dissolve 0.133 gram of $ZrOCL_2 \cdot 8H_2O$ in 25 milliliters of H_2O. Add 350 milliliters of concentrated HCl, and dilute to 500 milliliters with distilled water. This solution is stable at room temperature for at least three months.

Spadns reagent — Combine equal parts of the Spadns solution and $ZrOCL_2 \cdot 8H_2O$ solution, and mix thoroughly. This reagent is stable for at least 2 years.[3]

Reference solution — Dilute 7 milliliters of concentrated HCl to 10 milliliters with distilled water. Add 10 milliliters of Spadns solution to 100 milliliters of distilled water and add the HCl solution. Mix well. This solution is used to set the spectrophotometer zero point and is stable indefinitely.[24]

Standard fluoride solution — Dissolve 2.2105 grams of dry NaF, and dilute to 1 liter with distilled water. Dilute 1 milliliter of this solution to 1 liter. This final solution contains 1.0 micrograms per milliliter of fluoride.

Distillation procedure — Place 400 milliliters of water, 200 milliliters concentrated sulfuric acid, and about two dozen carborundum chips into the boiling flask and swirl to mix. Caution — the sulfuric acid water solution should be mixed thoroughly before heat is applied to prevent splattering. Connect the apparatus as shown in Figure B-8. Begin heating slowly at first, then rapidly until a temperature of 180° C has been reached.[23] The connection between the boiling flask and condenser must be separated immediately after the heat is removed to prevent suckback of the sample and for safety reasons. About 300 milliliters of water should have been distilled over in about 45 minutes. At this point, the apparatus has been flushed free of fluoride and the acid-H_2O ratio has been adjusted. When the flask has cooled to 120° C, the apparatus is ready for the sample.

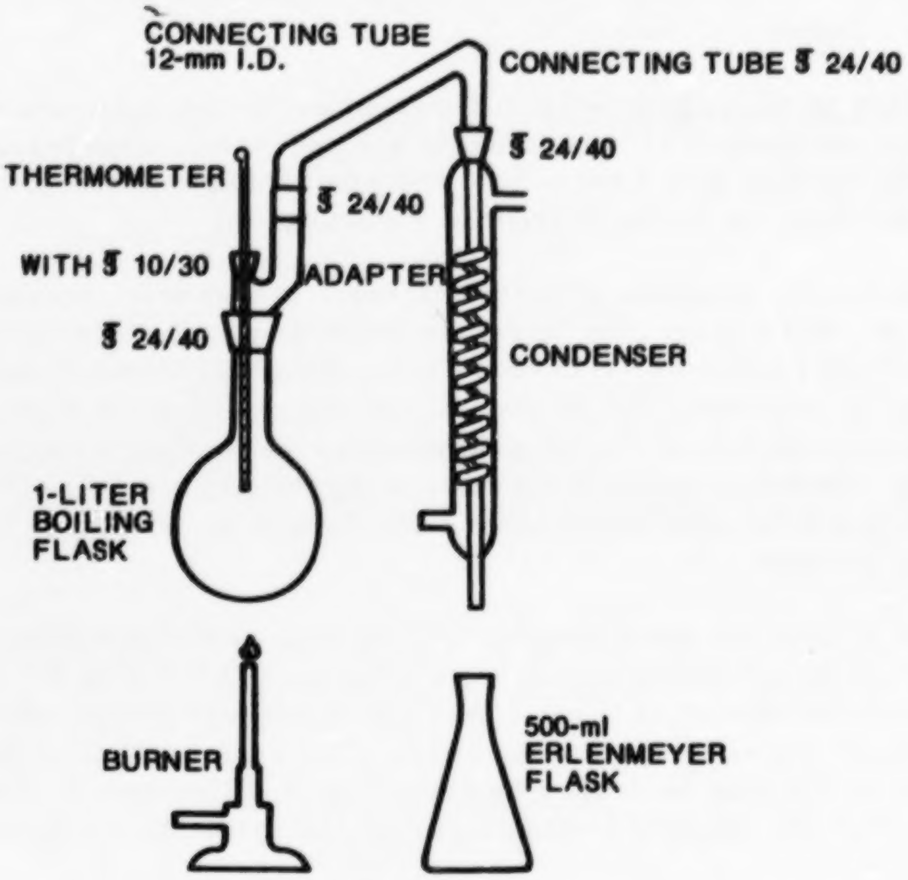


Figure B-8. Fluoride distillation apparatus.

Add 300 milliliters of distilled water containing an aliquot of the impinger sample, corresponding to 0.5 to 0.9 milligram of fluoride to the boiling flask, swirl to mix, and connect the apparatus and distill as before, until the distillation temperature reaches 180° C. For distillation of water-soluble particulate fluorides, take a suitable aliquot of the supernatent liquid of the particulate sample, dilute to 300 milliliters with distilled water, and add to the distillation flask. For distillation of total particulate fluorides, use a suitable aliquot of the water-soluble-plus water-insoluble sample. To obtain a representative sample, withdraw an aliquot using a calibrated, sawed-off pipette, immediately after intimate mixing of the sample. In no case should the aliquot contain more than 0.9 mg of fluoride. Distill the sample, as before, until a temperature of 180° C has been reached. Fluoride content of phosphate rock or fertilizer may be determined using these same procedures, provided the approximate percentage weight of fluoride in the sample is known so that the still is not overcharged. Weigh out a sample to the nearest 0.1 milligram, corresponding to about 0.5 milligram of fluoride, dilute to 300 milliliters with distilled water and distill as before until a temperature of 180° C has been reached. Pipet a suitable aliquot (containing 10 to 40 micrograms of fluoride) from the distillate and dilute to 50 milliliters. Add 10 milliliters of Spadns-reagent, mix thoroughly, and read the absorbance. If the absorbance falls beyond the calibration curve range, repeat the procedure using a smaller aliquot.

Discussion of procedure – The estimated error for the combined sampling and analytical procedure is ± 15 percent. The error of the analytical method is ± 4 percent. The spectrophotometric measurements should be reported to the nearest 0.5 microgram.

Aluminum, calcium, chloride, ferric, manganese, magnesium, phosphate, and sulfate ions interfere positively in the Spadns method.[1] These interferences are removed during the distillation of the sample. Chloride interference can be eliminated when present in high concentrations by the addition of 5-milligrams silver sulfate per milligram of chloride. Addition of a few crystals of Ag_2SO_4 to a small portion of the sample should be performed before distillation to determine if chloride ions are present.

The determination of fluorides using this procedure may be carried out at any temperature within the range of 15° to 30° C. The important consideration here is that standards and sample should be at nearly identical temperature, because an error of 0.01 milligram per liter of fluoride is caused by each degree difference in temperature.[2] Color, after the initial 15-minute period, is stable for about 2 hours.

When the fluoride content of the aliquot is above 0.9 milligram, the distillation apparatus should be purged with 300 milliliters of distilled water, so that there will be no residual fluoride carried over when the next sample is distilled. Keeping the fluoride content around 0.5 milligram eliminates the necessity of purging the distillation apparatus between samples. The acid need not be replaced until the accumulation of ions causes carry-over of interferences or retards fluoride recovery. An occasional recovery check with standard fluoride samples will indicate when the acid should be replaced.[22]

Calculations

$$\text{ppm fluoride} = \frac{44.82\ (C)\ \ (F)}{V_S}$$

where:

C = concentration fluoride in aliquot, milligram

F = dilution factor

V_S = volume of gas sample at 70° F and 29.92 in. Hg, scf

$$44.82 = \frac{\frac{530°R}{492°R} \times 22.4 \frac{\text{liters}}{\text{mole}} \times 10^6}{19 \frac{g}{\text{mole}} \times 10^3 \frac{mg}{g} \times 28.32 \frac{\text{liters}}{\text{cu ft}}}$$

Preparation of calibration curve - Pipet exactly 0.0, 10.0, 20.0, 30.0, 40.0, and 50.0 milliliters of standard NaF solution into separate 100-milliliter beakers. Add 50.0, 40.0, 30.0, 20.0, 10.0, and 0.0 milliliters of distilled H_2O respectively, to the beakers. Add 10 milliliters of Zirconyl-Spadns reagent to each beaker. Mix thoroughly and let stand for 15 minutes at room temperature. Set the instrument to zero absorbance using distilled water. Determine the absorptivity of the reference solution. The absorptivity of the reference solution should be in the range of 0.82 to 0.85, using 0.5-inch cells. Then, set the instrument to zero absorbance using the reference solution. Plot concentration versus absorbance on rectilinear graph paper.

APPENDIX C.

WET-PROCESS PHOSPHORIC ACID ESTABLISHMENTS IN UNITED STATES

The purpose of this tabulation of wet-process phosphoric acid manufacturing establishments (Table C-1) is to indicate the distribution and principal areas of concentration of this industry. The industry tends to be concentrated near the supply of phosphate rock; rock deposits are located in Florida, Tennessee, and the Idaho-Utah area.

Information was drawn from various sources and is believed to represent the operable installations existing as of May 1967. As a result of sale, merger or lease, some company identifications may differ from those presently in use, but this listing should serve the intended purpose of general identification.

Table C-1. WET-PROCESS PHOSPHORIC ACID ESTABLISHMENTS IN UNITED STATES (as of May 1967)

State	City	Company	Capacity, tons/yr (P_2O_5)
Arkansas	Helena	Arkla Chemical Corporation	
California	Bena	AFC Inc.	20,000
California	Dominquez	Western States Corporation	12,000
California	Helm	Valley Nitrogen Products, Inc.	60,000
California	Lathrop	The Best Fertilizers Corporation	20,000
California	Trona	American Potash and Chemical Corporation	5,000
Delaware	North Claymont	Allied Chemical Corporation	33,000
Florida	Bonnie	International Minerals and Chemicals Corp.	495,000
Florida	Bartow	Armour Agricultural Chemical Company	272,000
Florida	Bartow	Swift and Company	90,000
Florida	Brewster	American Cyanamid Company	200,000
Florida	Fort Meade	Armour Agricultural Chemical Company	165,000
Florida	Hamilton	Occidental Petroleum Company	550,000
Florida	Mulberry	F. S. Royster Guano Company	30,000
Florida	Nichols	Mobil Chemical	230,000
Florida	Pierce	Consumers Cooperative Association	75,000-100,000
Florida	Piney Point	Borden Chemical Company	140,000
Florida	Plant City	Borden Chemical Company	
Florida	Plant City	Central Phosphates	100,000
Florida	Ridgewood	W. R. Grace Company	165,000
Florida	South Pierce	American Agricultural Chemical Co.	228,000
Florida	Tampa	Tennessee Corporation, U. S. Phosphoric Products Division, Cities Service	340,000
Florida	Green Bay	Farmland Industries	110,000
Florida	White Springs	Occidental Agricultural	250,000
Idaho	Conda	El Paso Products Company	90,000
Idaho	Kellogg	The Bunker Hill Company	33,000
Idaho	Pocatello	J. R. Simplot Company	270,000
Illinois	Dupue	New Jersey Zinc Company	130,000
Illinois	E. St. Louis	Allied Chemical	35,000
Illinois	Joliet	Olin Mathieson Chemical Corporation	125,000

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Table C-1 (continued). WET-PROCESS PHOSPHORIC ACID ESTABLISHMENTS IN UNITED STATES (as of May 1967)

State	City	Company	Capacity, tons/yr (P_2O_5)
Illinois	Marseilles	National Phosphates (Hooker Chemical Corp.)	200,000
Illinois	Morris	Des Plaines Chemical (Stauffer Company)	90,000
Illinois	Streator	Borden Chemical Company	33,000
Illinois	Tuscola	U. S. Industrial Chemicals Corporation	30,000
Indiana	Gary	Socony Mobil Oil Company	40,000
Louisiana	Convent	Freeport Chemical	600,000
Louisiana	Geismar	Allied Chemical Corporation	180,000
Louisiana	Hahnville	Hooker Chemical Corporation	100,000-120,000
Minnesota	Pine Bend	Northwest Cooperative Mills, Inc.	54,000
Mississippi	Pascaugoula	Coastal Chemical Corporation, Inc.	50,000
Missouri	Joplin	Consumers Cooperative Association	53,000
Missouri	Joplin	Farmers Chemical Company	50,000
Missouri	Joplin	W. R. Grace Company	50,000
Missouri	Joplin	W. R. Grace Company	33,000
New Jersey	Paulsboro	Dixon Chemical Industries (not operating)	40,000
North Carolina	Aurora	Texas Gulf Sulphur	375,000
Oklahoma	Tulsa	Nipak, Inc.	30,000
Texas	Houston	Phosphates Chemical Inc. (Stauffer)	100,000
Texas	Pasadena	Olin Mathieson Chemical Corporation	200,000
Texas	Pasadena	Phosphate Chemicals Inc. (Stauffer)	80,000-100,000
Texas	Texas City	Borden Chemical Company	40,000
Utah	Garfield	Western Phosphates Inc. (Stauffer)	100, 00

APPENDIX D

PHYSICAL DATA ON PROPERTIES OF CHEMICALS AND SOLUTIONS RELATED TO WET-PROCESS PHOSPHORIC ACID MANUFACTURE

Table D-1. PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF PHOSPHORIC ACID[29]

Concentration, %		Density, g/cc	Boiling point, °C	Specific heat, cal/g[a]	Specific electrical conductivity, at 18 °C, mho
H_3PO_4	P_2O_5				
0	0	0.997	100.0	-	-
5	3.62	1.024	100.1	0.973	-
10	7.24	1.052	100.2	0.939	0.0566
20	14.49	1.113	100.8	0.871	0.1129
30	21.73	1.180	101.8	0.798	0.1654
50	36.22	1.332	108	0.656	0.2073
75	54.32	1.574	135	0.542	0.1209
85	61.57	1.685	158	0.493	0.0780
100	72.43	1.864	261	-	-
115	83.29	2.044	-	-	-

[a] Average value from 20° to 120°C.

Table D-2. KINEMATIC VISCOSITY OF PHOSPHORIC ACID SOLUTIONS[29]
(centistokes)

Concentration, % H_3PO_4	Temperature, °C							
	20	30	40	60	80	100	140	180
0	1.0	0.80	0.66	0.48	0.37	0.30	-	-
5	1.1	0.89	0.74	0.54	0.42	0.33	-	-
10	1.2	0.99	0.83	0.61	0.47	0.38	-	-
20	1.6	1.3	1.1	0.78	0.60	0.48	-	-
30	2.2	1.7	1.4	1.0	0.79	0.62	-	-
50	4.3	3.3	2.6	1.8	1.4	1.1	-	-
75	15	10	7.8	4.8	3.3	2.4	-	-
85	28	19	14	8.1	5.1	3.8	2.2	-
100	140	81	53	25	14	9.2	4.5	2.9
115		-	-	1500	600	250	68	28

Table D-3. VAPOR PRESSURE OF PHOSPHORIC ACID SOLUTIONS[29]
(mm Hg)

Concentration, % H_3PO_4	Temperature, °C							
	20	30	40	60	80	100	110	140
0	17.6	31.8	55.3	150	355	760	1075	-
5	17.5	31.5	54.5	147	352	755	1068	-
10	17.3	31.0	54.2	146	350	753	1066	-
20	17.0	30.0	53.0	141	341	735	1040	-
30	16.3	28.9	50.5	136	327	705	996	-
50	13.0	23.1	40.3	108	257	575	814	-
75	5.65	10.0	17.5	47.0	111	240	340	895
85	2.16	3.95	6.95	19.7	48.8	111	160	445
100	0.0285	0.0595	0.120	0.430	1.33	3.65	5.80	20.3

Table D-4. PARTIAL PRESSURE OF HYDROGEN FLUORIDE OVER HF-H_2O SOLUTIONS[30]
(mm Hg)

Hydrogen fluoride, wt %	Temperature, °C					
	0	20	40	60	80	100
0	0	0	0	0	0	0
10	0.03	0.14	0.51	1.62	4.50	11.2
20	0.09	0.41	1.51	4.75	13.2	32.7
30	0.30	1.27	4.46	13.4	35.7	85.5
50	3.66	12.4	35.8	91.4	209	440
70	41.2	118	295	662	1355	2570
100	364	773	1516	2778	4801	7891

Table D-5. PARTIAL PRESSURE OF WATER OVER HF-H_2O SOLUTIONS[30]
(mm Hg)

Hydrogen fluoride, wt %	Temperature, °C					
	0	20	40	60	80	100
0	4.58	17.54	55.32	149.38	355.1	760.0
10	4.46	16.0	48.9	131	312	679
20	3.63	13.1	40.3	108	259	566
30	2.72	9.25	30.6	82.6	199	436
50	0.76	2.98	9.86	28.2	71.9	165
70	nil	0.1	......	......	......	......
100	0	0	0	0	0	0

Table D-6. VAPOR PRESSURE OF ANHYDROUS HYDROGEN FLUORIDE[31]

Temperature, °C	Vapor pressure, psia
-10	4.65
0	7.00
10	10.3
20	15.0
30	21.2
40	29.5
50	39.8
60	53.8
70	71.0

Table D-7. PHYSICAL PROPERTIES OF FLUORINE AND SILICON COMPOUNDS

SiF_4[11]

Boiling point	−95 °C
Density @ 0 °C, 1 atm	4.69 g/liter
C_p	18.2 cal/mol °C
Heat of formation	−370 K cal/g mol
ΔH_v @ 183 °K, 1320 mm	4.46 K cal/g mol

$\log p = 10.469 - \frac{1352.8}{T}$ = vapor pressure, mm Hg

H_2SiF_6

Density of water solutions, g/cc

% H_2SiF_6	6	14	22	30
d	1.0491	1.1190	1.1941	1.2742

pH of industrial aqueous H_2SiF_6 solutions[23]

wt % H_2SiF_6	1.0	0.1	0.01	0.001
pH	1.4	2.2	3.0	3.8

$SiF_4 + 2HF\ XH_2O = H_2SiF_6 + XH_2O$

$\Delta H = -67K$ cal/g mol

$SiF_4 + 2H_2O = 2\ H_2SiF_6\ (aq) + SiO_2$

$\Delta H = -556.2$ K cal/g mol

Azeotropes[33]

wt %

HF	H_2SiF_6	H_2O	P, mm Hg	B P , °C
38.26	-	61.74	750.2	112.0[a]
10	36	54	759.7	116.1
-	41	59	760	111.5[a]

[a] Azeotropes estimated from ternary phase diagram.

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16. Abstracts Wet-process acid is produced by treating fluorapatite ($Ca_{10}(PO_4)_6F_2$) or phosphate rock, with sulfuric acid. Phosphate rock must be finely ground to react properly with sulfuric acid, and standard control equipment is normally used to prevent objectionable dust emissions. The emissions of most concern are fluoride compounds liberated from the rock by the sulfuric acid. These consist of hydrogen fluoride, silicon tetrafluoride, and some products of reaction and decomposition of the latter. Most phosphate rock contains 3.5 to 4 percent fluorine, and half of this may be volatilized in the processing. This represents a large potential source of pollution. Because of the principal atmospheric contaminants generated in the process are gaseous fluorides, vapor scrubbing is universally employed to control emissions. Specific devices used for control include venturi scrubbers, impingement scrubbers, and various kinds of spray towers. The results of MCA-PHS stack tests on ten wet-process phosphoric acid plants in various parts of the country are tabulated. The major source of gaseous fluoride emissions in wet-process phosphoric acid plant is the digester. Only trace quantities of particulate fluorides are normally present in exit gases from digesters and filters, and these can be removed effectively by scrubbing.

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